ISOTOPES AND RADIATION TECHNOLOGY

A Quarterly Technical Progress Review

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Isotopes and Radiation Technology

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Isotopes and Radiation Technology

is a Technical Progress Review prepared by the Isotopes Information Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

Insofar as feasible all references are checked by the editors, using the library facilities of Oak Ridge National Laboratory, Oak Ridge Associated Universities, and the University of Tennessee. Occasionally, however, the cited material is not available; such cases are identified by an asterisk (*).

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development
Isotope Technology Development
Food Irradiation
Process Radiation Development
Source Development
Isotopic Heat and Power Development
Applications in Life Sciences
Safety
Isotopes Around the World
Miscellaneous

P. S. Baker, Robert H. Lafferty, Jr., Martha Gerrard, R. E. Greene, F. E. McKinney, Joan E. Carden, F. J. Miller, and D. N. Hess, *Editors*
A. F. Rupp, *Adviser*

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The United States Atomic Energy Commission publishes the Technical Progress Reviews to meet the needs of industry and government for concise summaries of current nuclear developments. Each journal digests and evaluates the latest findings in a specific area of nuclear technology and science. *Nuclear Safety* is a bimonthly journal; the other three are quarterly journals.

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Nuclear Safety
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Other U. S. Government agency reports identified in this journal generally are available from CFSTI.

Private-organization reports should be requested from the originator.

United Kingdom Atomic Energy Authority (UKAEA) and Atomic Energy of Canada Limited (AECL) reports are available at USAEC depository libraries. UKAEA reports are sold by Her Majesty's Stationery Office, London; AECL reports are sold by the Scientific Document Distribution Office, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada. UKAEA and AECL reports issued after March 1, 1967, are sold by CFSTI to purchasers in the United States and its territories.

Section

I

Isotopes and Radiation Technology

Isotope Production and Development

The Enrichment of Radioactive ^{85}Kr

By W. R. Rathkamp*

Abstract: *The Oak Ridge National Laboratory thermal-diffusion pilot plant for enriching radioactive ^{85}Kr to approximately 40% is described.*

In 1956 a program was started at Oak Ridge National Laboratory (ORNL) to make available the enriched isotopes of the noble gases.[1] The thermal-diffusion process was chosen, since it is one of the very few isotope-enrichment methods applicable to the small-scale processing of inert gases. As responsibility for satisfying demands for these separated stable isotopes was transferred to Mound Laboratory, emphasis at ORNL shifted toward the enrichment of radioactive isotopes such as ^{85}Kr. Figure 1 shows visually the effects of enriched krypton and demonstrates what can be accomplished in the application of beta-stimulated phosphors as light sources. This photograph shows two glass capillary tubes containing identical powdered phosphor and filled to the same pressure with krypton gas, the gas in one tube having normal 3.6% ^{85}Kr content and the gas in the other having enriched 27.6% ^{85}Kr content.

Thermal Diffusion

The principle of thermal diffusion has been thoroughly studied and the theory discussed by a number of investigators, including Jones and Furry,[2] Grew,[3] and Von Halle.[4]

Principle of Operation

A thermal-diffusion column consists fundamentally of a hot wall and a cold wall, separated by a small distance and arranged in a vertical plane. The process gas or gases occupy the space between these walls. The countercurrent phases consist of an upward-moving layer of hot gas rising along the heated wall and a downward-moving layer of cold gas falling along the cooled wall. Normal convection keeps these currents moving continuously in opposite directions. Thermal diffusion creates a small tendency for the lighter molecules to drift toward the hot region where they are carried upward by the rising convection stream, and for the heavier molecules to drift toward the cold region where they are carried downward by the falling stream. This small separation effect is magnified, by the countercurrent flow, into a large enrichment that is realized in a vertical direction. In most cases it is more practical to construct a thermal-diffusion system with the walls as concentric cylinders rather than as parallel plates, i.e., a tubular heater within a cooled tube. Such an arrangement is used in the ^{85}Kr pilot plant at ORNL.

The thermal-diffusion column of the type first described in 1938 by Clusius and Dickel[5] and used in modified form at ORNL is actually a countercurrent extraction process in which a small separation factor is maintained between two phases as these phases are moved continuously in opposite directions. Gas–liquid and immiscible liquid–liquid extraction systems are well known, but the concept of a gas–gas extraction system may be a little difficult to grasp, particularly if both gas phases are of the same element and differ only in their isotopic distributions. If one is separating dissimilar gases by thermal diffusion, the two phases will be chemically different, but if one is enriching isotopes of a single gas, the countercurrent phases are not chemically identifiable and consist only of a hot-gas phase and a cold-gas phase. As is true for most isotope

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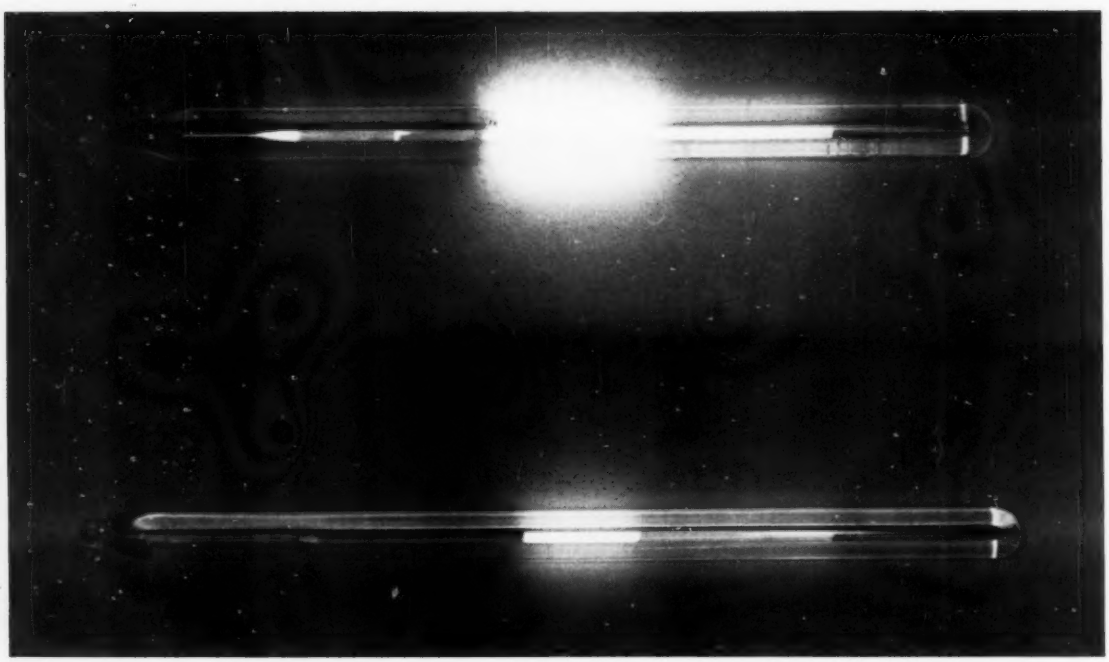

Fig. 1 Effect of enrichment of ^{85}Kr on intensity of light from a phosphor. At bottom, 3.6% ^{85}Kr; at top, 28% ^{85}Kr.

separation systems, thermal diffusion deals with extremely weak forces and very delicate and sensitive mechanisms.

^{85}Kr Enrichment

Fission-product krypton, as recovered from uranium reactor fuel elements, consists mainly of a mixture of four stable and one (mass 85) long-lived radioactive isotopes. Although the exact composition of fission krypton depends upon the operating conditions in the reactor and the age of the fuel elements, typical isotopic concentrations are: mass 86—51.5%, mass 85—3.6%, mass 84—30.2%, mass 83—13.8%, mass 82—0.76%, and traces of the lighter masses 80 and 78.

The enrichment of ^{85}Kr is particularly difficult since this isotope is neither the heaviest nor the lightest mass in the fission-product gas, and krypton is not as easily separated by thermal diffusion as the lighter noble gases. However, on the basis of 10 years' experience with the successful enrichment of the "end isotopes" (mass 86 and 78) of stable krypton and of the "middle isotopes" ^{21}Ne and ^{38}Ar, a thermal-diffusion system was designed to enrich ^{85}Kr from its available concentration of approximately 4% (70 curies/liter) in fission-product gas to 15% in one stage of operation or to 40% in a two-pass, batch operation.

Column Bundles

The basic unit of this enrichment plant is a bundle of columns very similar in appearance to a common heat exchanger; it is approximately 8 ft long and 10 in. in outside shell diameter, containing 36 independent tubes (Fig. 2). Each of these tubes consists of a 7-ft 9-in. length of stainless-steel tubing ¾ in. in outside diameter and 0.020 in. in wall thickness with a 0.440-in.-diameter tubular heater maintained coaxially within the tube by triangular steel spacers. The process gas, krypton, occupies the annular space between the heater and the tube while cooling water flows between the outside of the tubes and the heat-exchanger shell. All 36 tubes in a bundle are connected in series, top of one tube to bottom of the next, with ⅛-in.-ID copper tubing to give one effective thermal-diffusion column with a total length of 279 ft (Fig. 3). Gas transport through these lines and between columns is provided by a bellows pump connected across the extreme ends

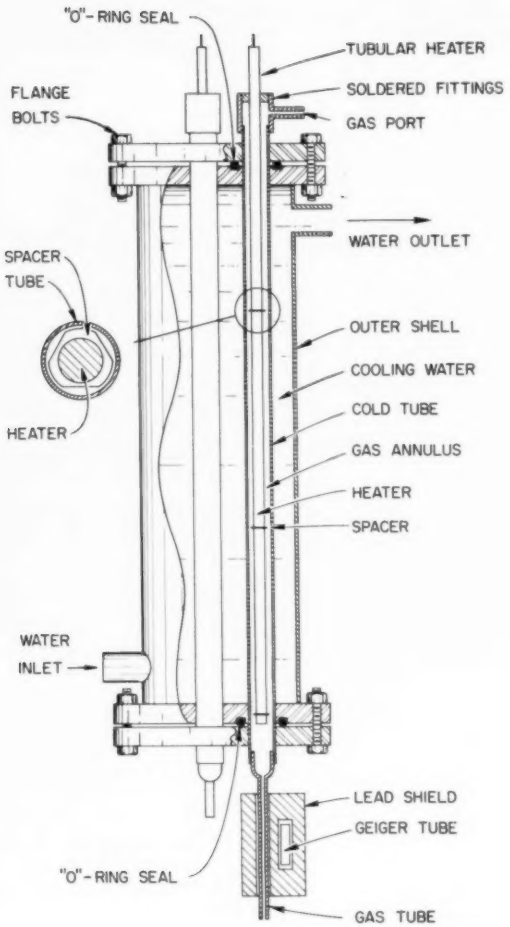

Fig. 2 36-tube thermal-diffusion column bundle.

of the series of columns. This pump alternately compresses and expands two metal bellows to displace about 50 ml of gas back and forth throughout the entire system on a cycle of once every 15 min. In each bundle, four Geiger tubes are arranged along the length of the tubes to monitor the movement of the radioactive isotope within the system and to permit the enrichment and depletion profiles to be measured and plotted continuously during operation. A liquid-nitrogen trap is provided inside the cell for each bundle to allow gas transfers to be made into or out of the system by cryogenic pumping.

Three of these 36-tube bundles are installed in each of two cells approximately 4 × 6 ft in floor area and 10 ft in height, with concrete cell walls 2 ft thick to provide shielding against the 0.5-Mev gamma emission from the ^{85}Kr. The six units are operated independently; hence various concentration levels of radioactive krypton can be processed simultaneously in different units.

Operating Characteristics

If a thermal-diffusion system such as the 36-tube group used at ORNL is evacuated and filled with fission krypton, the cooling water and heater power turned on, and the system operated until essential equilibrium conditions prevail, the various isotopic species will tend to separate from one another and will redistribute themselves along the length of the system (Fig. 4). The line of short alternating black and white lines across the top of the figure represents the 36 individual columns in series; the line of five long alternating lines represents the sections of the plant which may be isolated and the contents of each withdrawn independently. It may be noted that the maximum in the ^{85}Kr concentration curve does not occur at the exact center of the system, but is displaced toward the light end and nearly out of the four-column center section represented in Fig. 4 by the center black line plotted across the top of the figure. This isotope peak can be easily shifted to the center by withdrawing a small amount of material from the heavy end of the system. The body of gas in the column will then expand proportionately toward this end and shift all the peaks while they maintain their relative positions.

Figure 5 shows the ^{85}Kr concentration curve at equilibrium and centered in the system. This figure shows the effect of withdrawing various amounts of material from the center of the string of columns. If the contents of the central four columns (approximately 1 liter of gas at 1 atm pressure) are isolated and withdrawn, an average mass-85 concentration of 15.8% will be obtained. If the contents of the central eight columns are withdrawn, twice the volume of gas will be obtained, but the average radioactive-mass concentration in this total gas will fall to 12.5%. As the center cut withdrawn is widened still further, the average concentration obtained will continue to decrease.

Table 1 shows the effect of withdrawing various cut widths and lists the average ^{85}Kr concentration obtained, the corresponding specific activity, the total volume of gas withdrawn, and the percent of the total activity in the system which is recovered by a withdrawal of a given amount from the center of the system.

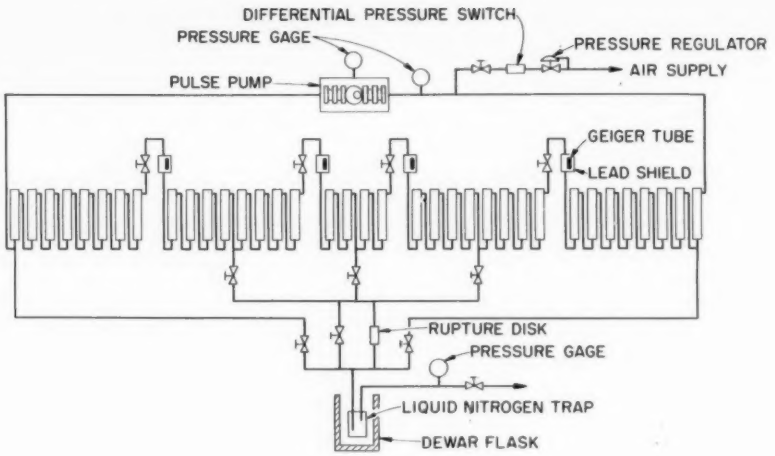

Fig. 3 36-tube thermal-diffusion column bundle showing schematic column and piping arrangement.

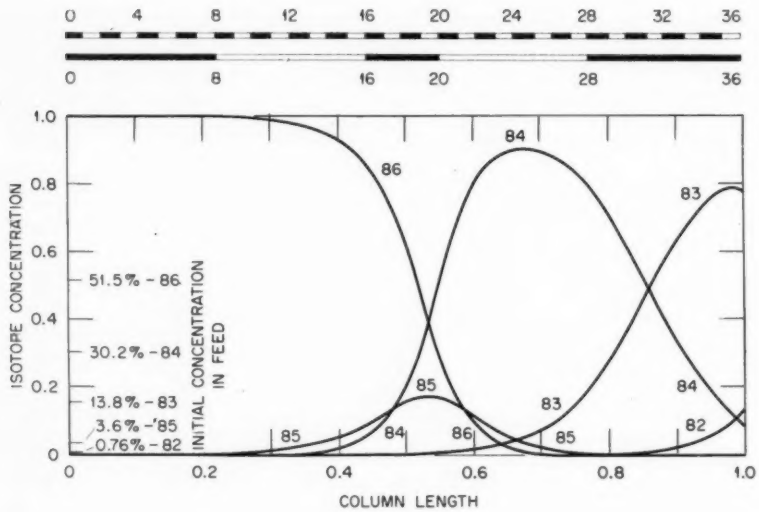

Fig. 4 Isotope distribution in 36-tube thermal-diffusion system at equilibrium; first-pass feed material, 3.6% ^{85}Kr.

The concentration distributions of ^{85}Kr in second-pass operation using various cuts of feed material obtained from a first pass are shown in Fig. 6. The final product concentration withdrawn from the four center tubes of the second-pass operation is increased if feed material of increased ^{85}Kr concentration is used. However, there are some equipment limitations if high-level ^{85}Kr is desired as feed for the second pass. About 9 liters of gas is required to fill a 36-tube bundle, and it can be seen from Table 1 that only two batches of 6.5% ^{85}Kr obtained in first-pass center cuts of 20 columns each provide enough gas to fill a second pass, whereas nine batches of 15.8% ^{85}Kr obtained from first-pass cuts of 4 columns each are required for a second-pass charge. Two consecutive runs of approximately 60 days each will be required to obtain this high-level research material, since only six thermal-diffusion units are available in the pilot plant. Another consideration, in addition to the time required to accumulate sufficient feed material, is the storage of this first-pass product as well as of the partially enriched tailings left in the system after the 4-column product is removed.

Production

The ^{85}Kr thermal-diffusion pilot plant has produced to date 1460 curies of 15% ^{85}Kr by single-pass

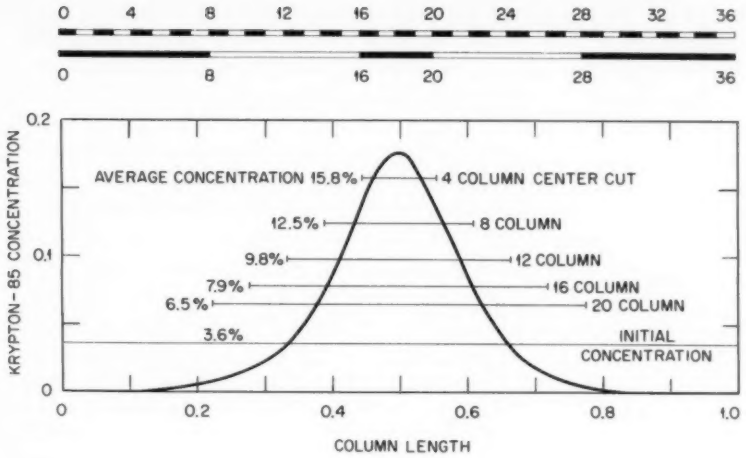

Fig. 5 ^{85}Kr distribution in 36-tube thermal-diffusion system at equilibrium, first pass, with the feed material 3.6% ^{85}Kr. Shown is the average ^{85}Kr concentration obtained in center cuts of various lengths.

Table 1

Number of columns withdrawn	Average ^{85}Kr concentration, %	Specific activity, curies/liter	Volume of gas, liters	Fraction of total activity, %
4	15.8	276	1	48.6
8	12.5	219	2	76.9
12	9.8	172	3	90.5
16	7.9	138	4	97.2
20	6.5	114	5	99.9

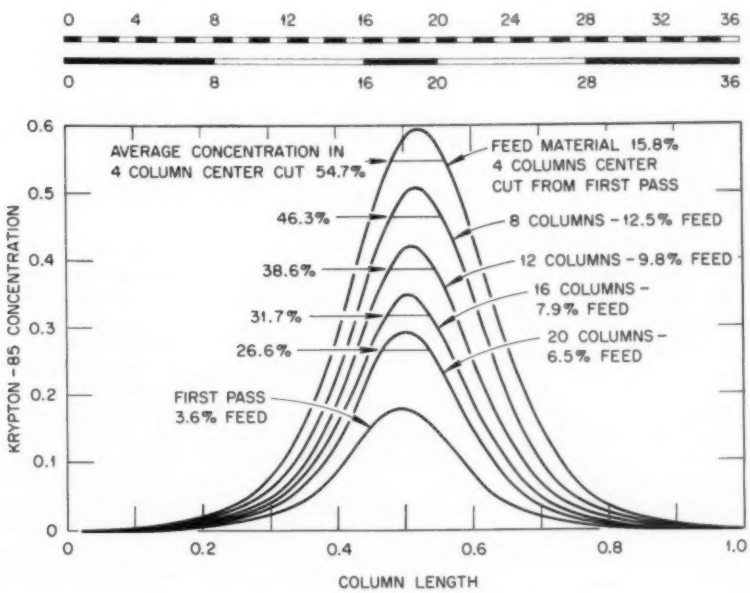

Fig. 6 ^{85}Kr distribution in 36-tube thermal-diffusion system at equilibrium, second pass, with the feed material various center cuts from the first pass.

operation and 370 curies of material containing 27.6% ^{85}Kr by a second-pass enrichment of partially concentrated material obtained as a by-product of the 15% enrichment runs. This enrichment plant will continue to operate in the future producing 15% and eventually the full 40% design concentration of ^{85}Kr.

Safety Considerations

A number of safety features are incorporated into the system to prevent damage to the equipment or loss of gas if a malfunction should occur: (1) During transfer operations, a large amount of gas is often frozen in the liquid-nitrogen trap. If the trap should warm up with the inlet and outlet valves closed, dangerous pressures could develop; so a rupture disk is provided to vent this pressure back into part of the cascade. (2) Since the metal bellows used in the pulse pump has a definite lifetime and will crack eventually, the pump is enclosed in a gastight housing. A bellows failure will release some gas into this housing, and the resulting pressure rise will be indicated by a pressure gage. (3) If the cooling-water circulation should be interrupted, the tube bundles would overheat, with possibly deleterious results. A thermal switch is mounted on each tube bundle to automatically turn off the heaters if the water temperature exceeds a preset limit. (4) A gas leak out of the system will cause a drop in pressure, and a cooling-water leak into the system will cause a rise in pressure. If the gas pressure should increase or decrease beyond preset limits, a differential-pressure switch will sound an alarm. Any escape of gas too small to activate the pressure switch will be detected by very sensitive radiation-monitoring equipment installed in the cell-ventilation system, and an alarm will be given. (PSB)

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Large-Scale Exploitation of Fission-Product Rhodium and Palladium*

By C. A. Rohrmann†

Abstract: *The rare and valuable noble metals rhodium and palladium are among those elements produced in highest yield in the fission process, particularly in the fission of plutonium. The anticipated growth of the atomic power industry is at such a rate that within 10 years the discharge of wastes from the chemical processing of spent fuels from U. S. power reactors will contain more rhodium than is now supplied annually to American industry from conventional mineral sources. A similar situation should exist for palladium before the turn of the century. In addition, the few residual radioactive isotopes of rhodium and palladium known to be present in spent fuel are of such low concentrations, low activities, or low energies that expectations are promising for application of these isotopes in the important major large-scale uses. The large-scale exploitation of these elements from this new (and until recently nonexistent) source affords a possible ever-growing supply of these precious metals to serve mankind's essential needs, e.g., as catalysts in fertilizer production and as materials for communications equipment.*

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†Consultant, Chemistry and Metallurgy Division, Pacific Northwest Laboratory (Battelle–Northwest), Battelle Memorial Institute, Richland, Wash., a prime contractor for the USAEC.

The term "fission product" generally brings to mind thoughts of highly radioactive, hazardous waste materials requiring enormous efforts for safe disposal. Cursory inspection of a chart of the nuclides will show, however, that even after a rather short time—well within the time between fuel discharge from a reactor and the processing of this fuel—some fission products exist as stable elements like those found in nature, e.g., Ba, La, Pr, and Nd. But, in general, such materials are of insufficient value to justify recovery by the very costly processes required for highly radioactive wastes. The highly radioactive, unique, and potentially useful fission products such as ^{90}Sr and ^{137}Cs, and isotopes of the heavier elements such as Np, Am, and Cm, may, however, justify recovery under some circumstances. In addition to these by-products, there are a few that are of sufficiently low radioactivity and of such great real and immediate value that intensive recovery efforts may be justified and, indeed, possibly essential to the future welfare of mankind. These include fission-product rhodium and palladium.* The market prices of both these elements have increased significantly in the past few years and are now about $8 and $1.50 per gram ($249 and $47 per troy ounce), respectively. In addition, among all the potentially useful fission products, these elements have high fission yields, particularly in recycled plutonium fuels. Finally, the demand for these two elements is increasing greatly and reserves are shrinking. The recovery of these precious fission-product elements has been recognized as an economic potential for many years. Glueckauf[1] considered this possibility in 1955, and Engelhard Industries, Inc., obtained two patents[2] on processes for such recovery in 1963.

Natural Rhodium and Palladium

Both rhodium and palladium are members of the group called the "noble" or "platinum" metals, which also includes iridium, osmium, platinum, and ruthenium. The recent annual world production[3] of all these elements has been some 70 to 100 short tons (2 to 3 million troy oz). Although they have been recovered in placer mining, the free world's present supply,[4] including those recovered as by-products of such mining for gold in many parts of the world, comes almost entirely from the copper–nickel ores of Canada (32%) and South Africa (43%), with occasional very large purchases from Russia (20%). Some of the South African copper–nickel ores are sufficiently rich in platinum to justify processing for the noble metals alone. Russian production was formerly from extensive placer operations in the Ural Mountains, but it now is reported to be largely from ores of the Kola Peninsula and of Noril'sk in northwestern Siberia, where the mineralization is understood to be similar to that of the South African sources. However, the exact source and the magnitude of Russian reserves, though probably large, are not generally known to the free world.[5]

The distribution of the individual noble metals in various ore bodies differs widely. Canadian sources yield metal that is about 40% platinum and 40% palladium, the balance being rhodium, ruthenium, and iridium.[3] African ores, on the other hand, yield metal that is about 72% platinum and 25% palladium,[5] while Russian ores yield metal that is reported to be 60% palladium, 30% platinum, and 10% other members of the group.[6] Russia produces about half the world's total supply of the noble metals and is second to South Africa in the production of platinum alone.[3] Thus in view of the relatively low ratio of platinum to the other noble metals in known Russian ore sources, Russia apparently produces very substantial quantities of the other platinum metals and is estimated to supply 80% of the world's palladium[5] and 75% of the free world's supply of rhodium.[7] The total world reserves of recoverable platinum-group metals, 40% of which are in South Africa, are reported[4†] (in troy ounces‡) to be 15 million for platinum, 7.5 million for palladium, and 2.5 million for others of the group.

According to Day[8] the concentrations of these metals in the earth's crust are

Element	g/ton	%	Element	g/ton	%
Pt	0.005	5×10^{-7}	Pd	0.01	1×10^{-6}
Ir	0.001	1×10^{-7}	Rh	0.001	1×10^{-7}
Os	0.001	1×10^{-7}	Ru	0.001	1×10^{-7}

*It is concluded that of all the fission products (and nonfissionable neutron-addition products) available on a large scale from reactor operations, rhodium and palladium are, today, the only ones for which a ready market, and, more significantly, important and compelling needs already exist.

†These figures must now be concluded to be low in view of details presented in Ref. 6.

‡One troy ounce = 1.097 avoirdupois ounces = 31.10 g. In world markets, platinum-group metals are measured in kilograms, but, where the British system of weights prevails, the troy ounce is used. One kilogram equals 32.15 troy ounces. In the United States the troy ounce is used exclusively.[5]

It should be noted that this distribution is far different from that shown for the recoverable reserves. In general, on the basis of reported production, imports, and consumption, the quantity of palladium is larger than that of any of the other of these metals and generally about twice that of platinum.[6] Rhodium ranges from 4 to 12% of the combined amount of platinum and palladium. It is followed closely by iridium and then by much smaller fractions of ruthenium and osmium. Insofar as availability is concerned, osmium is the rarest.

In nature rhodium consists only of the nuclide ^{103}Rh. The isotopic composition of palladium is

Isotope	Abundance, at.%	Isotope	Abundance, at.%
^{102}Pd	0.96	^{106}Pd	27.33
^{104}Pd	10.97	^{108}Pd	26.71
^{105}Pd	22.23	^{110}Pd	11.81

Rhodium Uses

The annual demand for rhodium in the United States has been (from data in appropriate issues of *Minerals Yearbook* and other more recent Bureau of Mines data):

Year	Demand, troy oz	Year	Demand, troy oz
1956–1960, average	21,805	1964	55,426*
1961	19,174	1965	38,910
1962	26,063	1966	69,688*
1963	37,068	1967	54,952

*Includes a major substitution in the glass industry because of the unavailability of platinum.

Rhodium is used mainly in the chemical, glass, and electrical industries and for jewelry and decorative applications. Rhodium demands by various industries (also from data in *Minerals Yearbook* and other more recent Bureau of Mines data) in recent years are shown in Table 1.

The use for rhodium in the chemical industry is almost entirely for nitric acid production, where it serves to improve the durability, and thus the useful lifetime, of the platinum catalyst in the ammonia oxidation process. This catalyst is used[9] in the form of a multilayer gauze of woven wire (90% Pt–10% Rh). The wire is 0.06 mm in diameter, and the gauze is woven to give 1024 apertures/cm^2. The catalyst assembly generally consists of 3 to 5 (and in some installations up to 40) layers of gauze.[10] For large low-pressure plants the diameter of the gauze pad may be as much as 12 ft and the operating temperatures as high as 950°C.

A modern high-pressure nitric acid plant with 300 tons/day capacity requires about 20 kg† of gauze in service with approximately the same amount kept on hand for replacement of spent gauze. It may be assumed that the supplier has a like amount also, either in process (as spent gauze and reclaimed residues) or as inventory, to ensure prompt service to his customer. Thus, each such acid plant is supported by a total of about 60 kg of gauze, 6 kg of which is rhodium valued at about $50 thousand as commercial rhodium.

With expanding world food demands, a greatly increasing dependence is being placed on fertilizers to increase the yield of food grains throughout the world. The world's production[9] of nitric acid for the manufacture of ammonium nitrate fertilizer is greatly expanding and now exceeds 20 million metric tons/year. All this production and continued expansion

†Estimated from data in Ref. 10.

Table 1 Industrial and Other Demands for Rhodium in the United States

Industry	Demand, troy oz					
	1962	1963	1964	1965	1966	1967
Chemical	8,276	9,537	13,179	12,499	14,210	17,770
Glass	5,111	13,191	23,923	10,275	34,491	11,281
Electrical	5,265	6,676	7,687	7,924	9,216	11,736
Jewelry and decorative	6,546	7,044	8,296	7,498	9,100	8,775
Other	865	620	2,341	714	2,671	5,390
Total	26,063	37,068	55,426	38,910	69,688	54,952

are dependent on the economic availability of platinum and rhodium.

Palladium Uses

The total annual consumption of palladium in the United States has been (from data in appropriate issues of *Minerals Yearbook* and other more recent Bureau of Mines data):

Year	Consumption, troy oz	Year	Consumption, troy oz
1956–1960, average	412,935	1964	591,432
1961	508,040	1965	717,085
1962	519,860	1966	894,212
1963	526,527	1967	621,141

In the electrical industry, the principal use of palladium is in contact points for low-voltage switchgear[5] in the communications field, mainly in telephone relay switches. In the chemical industry, it is used in the purification of hydrogen and as a catalyst[3] for many reactions; it may in some instances be substituted for platinum, particularly in the petroleum industry.[7]

It is used mainly in the chemical, electrical, and medical–dental fields. The recent annual use (also from data in issues of *Minerals Yearbook* and other more recent Bureau of Mines data) in the United States is shown in Table 2.

Prices of Platinum-Group Metals

The prices (from data in appropriate issues of *Engineering and Mining Journal*) for the platinum metals since 1958 are shown in Table 3.

Fission-Product Rhodium and Palladium

Rhodium

A chart of the nuclides shows that there are 15 isotopes of rhodium, only one of which is stable. This stable isotope, ^{103}Rh, is also a fission product produced in fairly high yield (2.9% from ^{235}U and 5.6% from ^{239}Pu). All other fission-product isotopes of rhodium have extremely short half-lives—from a few seconds to a maximum of 36 hr. However, three isotopes or isomers of appreciable half-life are produced by $(n,2n)$ or $(n,3n)$ reactions with the stable ^{103}Rh; i.e., ^{102}Rh, which exists as the 206-day and 2.9-year isomers, and a 3.3-year ^{101}Rh isomer. Because of the rarity of its potential formation route, ^{101}Rh

Table 2 Industrial and Other Demands for Palladium in the United States

Field	Demand, troy oz					
	1962	1963	1964	1965	1966	1967
Chemical	110,518	118,757	117,102	156,796	221,559	192,011
Electrical	327,788	331,868	350,889	430,384	531,545	324,684
Medical–dental	54,899	42,940	49,893	50,192	67,102	56,085
Other	26,655	32,962	73,548	79,713	74,006	48,361
Total	519,860	526,527	591,432	717,085	894,212	621,141

Table 3 Prices of the Platinum-Group Metals

Metal	Price, dollars/troy oz										
	1958	1959	1960	1961	1962	1963	1964	1965	1966	1967	1968
Rhodium	125	125	125	140	140	140	145	185	200	225	250
Palladium	22.50	17	26	26	26	24	30	34	34	39	46
Platinum	80	55	85	85	85	80	90	100	100	112	123
Iridium	110	80	80	80	75	75	75	95	145	190	190
Ruthenium	55	55	60	60	60	60	60	60	60	60	60
Osmium	100	90	90	90	70	70	70	275	350	450	450

can probably be neglected. The two ^{102}Rh isomers are, however, readily identified in spent fuel from reactors. Although their concentrations are low, both emit gamma rays of appreciable energy. Thus concentrations would have to be extremely low before recovered rhodium could be considered for any normal commercial uses. Aging alone would lower the 206-day ^{102}Rh concentrations to acceptable levels. Aging for 5 to 6 years would reduce the concentration of this isotope by a factor of 10^3, but aging alone does not seem to be a practical way to eliminate the 2.9-year ^{102}Rh. Although analytical results have not been obtained on power-reactor fuels, rhodium recovered from aged production-reactor fuel-processing wastes at Battelle–Northwest have shown the 2.9-year ^{102}Rh concentration to be 5 to 10 μc per gram of total rhodium. If a similar situation prevails for rhodium from power-reactor-fuel waste, this level of activity may be tolerable for large-scale industrial applications, such as ammonia oxidation, where objectionable carry-over of active rhodium from the very durable Pt–Rh alloy catalyst into the product is not likely. However, before extensive consideration of such recovery and use can be seriously proposed, an extensive and detailed analysis and evaluation of rhodium recovery from typical power-reactor fuels will have to be made.

There is no question at this time about the quantities of rhodium available in spent fuels from power reactors. Low-enrichment thermal-power-reactor fuels exposed to 25 thousand Mwd/metric ton should have[11] a rhodium concentration of 335 to 480 g (10 to 16 troy oz) per metric ton, with the larger figures representing production under conditions of plutonium recycle. Studies that have been made to date show conclusively that in the year 1978—less than 10 years from now—about as much rhodium will be sent to underground storage in the form of wastes from nuclear power-reactor-fuel processing as is now normally mined worldwide for marketing in the United States in an average year[12,13] (Fig. 1).

On the basis that an adequate supply of platinum will be available from conventional sources and that fission-product rhodium derived (at 90% yield) from spent fuel from power reactors would be satisfactory for nitric acid production, then merely 20 tons of such fuel would provide the rhodium necessary to support one new, large (300 tons/day) nitric acid plant each year. From another viewpoint, such new nitric acid plant capacity would also be supported by rhodium recoverable from the fuel discharged annually from one 500-Mw(e) nuclear power plant of present design, fuel composition, and operating characteristics. If the 500-Mw(e) nuclear power plant should operate totally on recycled plutonium, it, alone, could provide the rhodium required for the startup and maintenance of three new nitric acid plants about every 2 years. Such nuclear production will be only 0.33% of the capacity expected to be in operation in 1980.

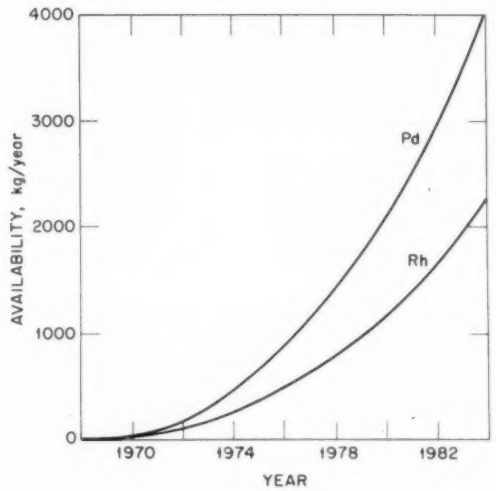

Fig. 1 Net annual availability of rhodium and palladium from U. S. power-reactor fuels.[13] Based on 90% recovery 1 year after discharge.

At present, the world's production of rhodium is entirely dependent on its recovery as a by-product from operations intended for the production of platinum. The same situation applies to each of the other platinum-group metals. The principal uses for rhodium, however, involve Pt–Rh alloys. Since uses for such alloys can be expected to increase—particularly in the nitric acid industry—it is entirely conceivable that future expansion of this industry could be inhibited by the scarcity of rhodium. This could, in turn, have a serious and unfavorable impact on fertilizer, and therefore food, production. The recovery and utilization of fission-product rhodium in conventional ways would ensure the continued and expanded availability of cheap fertilizers essential to the world's food supply.

Fixed-nitrogen fertilizers can be obtained without dependence on precious-metal-catalyzed ammonia oxidation, e.g., from the air–arc process from mineral-derived sodium nitrate, or from synthetic urea or cyanamide. However, since only in special and gener-

ally limited circumstances can these be as economical as the fertilizer based on the cheapest nitrates obtained by precious-metal-catalyzed ammonia oxidation, the latter is unlikely to be displaced in the forseeable future.

Palladium

The isotopic composition of natural palladium and that determined for fission-product palladium from reactor fuel are

Isotope	Composition, at.%	
	Natural	Fission product
^{102}Pd	0.96	–
^{104}Pd	10.97	1.4
^{105}Pd	22.23	48.9
^{106}Pd	27.33	22.4
^{107}Pd	None	15.7 (half-life, 7×10^6 years; 0.035-Mev beta)
^{108}Pd	26.71	8.9
^{110}Pd	11.81	2.7

Except for ^{107}Pd, the radioactive isotopes of palladium have such short half-lives that essentially no activity will be present in typical processed fuel. Power-reactor fuels exposed to 25 thousand Mwd/metric ton should have a palladium concentration of 880 to 1660 g (28 to 54 troy oz) per metric ton.[11]

Assuming that it has the above composition, palladium recovered from power-reactor fuels will have an activity of about 80 μc per gram of product. Although to some this may appear to be an intolerable activity for uncontrolled use, the beta energy is so low and palladium is such an inert and biologically unreactive element that activity expressed as curies is not a satisfactory measure of its hazard. At Battelle–Northwest palladium has been accurately determined in some power-reactor fuels.[14] Some palladium has been recovered from Hanford wastes and has shown no detectable activity. These observations seem to support expectations for suitability of recovered fission-product palladium for large-scale, uncontrolled industrial uses. However, as with rhodium, before extensive consideration of such recovery and use can be seriously proposed, an extensive and detailed analysis and evaluation of palladium recovered from typical power-reactor fuels will have to be made. In contrast with the recovery of rhodium, the recovery of palladium from power-reactor fuel-processing wastes, though impressive in quantity, will not match the annual amounts obtained from mineral sources until after 1990. However, the future realization of such rather massive additions to the world's palladium resources should stimulate consideration of expanded uses, particularly in those applications where it may replace platinum, which, it is assumed, will continue to be in short supply.

Because of the similarity of these metals, it is felt that an integrated process for their concurrent recovery would contribute significantly to the realization of an economic recovery operation. In fact, because of related processing conditions, it may be opportune to consider also concurrent recovery of cesium and technetium with anticipated economic benefits to each product in view of the expected sharing of operating costs. Although the value of palladium is substantially less than that of rhodium, the threefold larger amounts of palladium that are available for recovery in spent fuels should contribute significantly to the cost-sharing advantage. (REG)

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Hungary Exports ^{115m}In Generator

MEDIMPEX, the Hungarian Trading Company for Pharmaceutical Products (P. O. Box 126, Budapest 5), is exporting a ^{115m}In generator. It consists of a shielded ion-exchange column on which ^{115}Cd (43-day) is sorbed. The daughter ^{115m}In (23-hr) is eluted with 15 ml of 0.15 *M* HCl, which is passed through at a rate of 1 ml/min. The carrier-free product is obtained in isotonic saline. (MG)

Section

II

Isotopes and Radiation Technology

Isotope Technology Development

Applications of Neutron Activation to On-Stream Analysis*

By J. R. Rhodes†

Abstract: *Neutron activation techniques for process analysis are reviewed. Some comments are made on applications of accelerator and radioisotope neutron sources and on detection of prompt or delayed gamma rays by spectrometric, coincidence, and anticoincidence counting techniques. Different methods of sample presentation are surveyed, including semi-automatic batch sampling, conveyor-belt presentation of bulk materials, and continuous presentation of liquids and slurries. Applications include determination of oxygen in steel, nitrogen in food products, fluorine in fluoride minerals, aluminum in bauxite and cement, silicon in iron and a number of ores, and copper in copper ores.*

Neutron activation is a widely used and rapidly developing laboratory technique for elemental analysis,[1,2] but applications in the severe industrial environment are more recent and, as yet, less common. Neutron activation techniques have considerable potential in industry, however, since they possess certain very marked advantages over conventional methods, particularly in on-line analysis. The relatively high penetrating power of both the incident neutrons and emitted gamma rays makes measurements of moving material in standard steel containers or on ordinary conveyor belts feasible. Special presentation cells with thin and/or transparent windows are not necessary. Also, the high penetration (up to several inches) minimizes errors due to heterogeneity in analysis of coarse granular solids and slurries with variable particle size. The weight of material being measured, whether a continuous or a batch sample, can often be made large enough to be representative of the process stream at that time, thus removing a very important source of sampling error in process analysis.

In other methods of analysis, severe interferences can be caused by changes in chemical composition of the sample matrix. Such interferences do not occur in activation analysis because the interactions are nuclear and thus not affected by perturbations of the electron orbitals.

After a brief résumé of the various techniques in use, the known literature is reviewed, and some current work is described.

Techniques

An activation-analysis system consists basically of a shielded space where samples can be reproducibly positioned for neutron irradiation, a sample transfer system where the time delay between irradiation and counting can be controlled, and a counting space where the characteristic gamma rays of interest are measured, usually with a shielded NaI(Tl) gamma-ray scintillation spectrometer.

In on-stream analysis the sample is continuously flowing between irradiation and measurement, and optimization of flow rates and residence times with respect to wanted and unwanted radioactivity has to be considered.

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Neutron Sources

Of the available neutron sources (reactors, accelerators, and radioisotopes), the use of reactors is ruled out for process control unless a nuclear reactor happens to be on site. Thus the best source of thermal neutrons is not available. Accelerator sources (neutron generators) are normally designed to produce 14-Mev neutrons by the reaction which takes place when a beam of deuterons, usually accelerated to 150 kv, strikes a titanium tritide target. Neutron outputs up to several times 10^{11} n/sec are obtained from commercially available machines using so-called pumped neutron tubes with demountable tritium targets. Sealed neutron tubes with outputs of up to 10^{11} n/sec are also available. These outputs of fast neutrons are entirely adequate to accomplish a wide range of element determinations with high sensitivity. Thermal-neutron activation is less favored because the necessary moderation of the neutrons reduces the flux by about two orders of magnitude.

One of the main problems with neutron generators is the need to change targets frequently or, with sealed tubes, the expense of buying a new tube. In laboratory analysis this is acceptable because a typical irradiation time is about 1 min per sample and the total duration of tube operation may be only 1 hr per day. However, on-stream analysis often demands 24-hr continuous operation, and changing neutron targets or tubes every few days can be expensive and tedious.

The emission of neutrons from radioisotope sources is, for all practical purposes, stable and can be chosen to have an effectively unlimited life. Thus they are very well suited to industrial conditions. Radioisotope (α,n) sources produce neutrons with a continuous range of energies up to about 10 Mev, the most probable energy being about 4 Mev. The highest outputs available are only a few times 10^8 n/sec, using several tens of curies of an alpha emitter, such as ^{241}Am, ^{228}Th, or ^{210}Po, intimately mixed with a beryllium target material. Antimony-124–Be (γ,n) sources (half-life, 60.2 days) gave similar outputs of much lower energy neutrons. Californium-252 (a spontaneous fission source, with corresponding neutron spectrum), which emits 2.3×10^9 n/(sec)(mg) and has a half-life of 2.55 years, may be available for activation analysis in the future and would solve many problems.

Sometimes the lower energy of the radioisotope source, compared with 14-Mev neutrons, can be used to advantage to prevent occurrence of a reaction having a higher threshold energy. Neutron generators can also be used in this way since the reaction of deuterons with a deuterium target produces 3-Mev neutrons.

Industrial applications have been limited mainly to determination of major elements with high cross sections, so the requirements for high neutron source outputs are not nearly so pressing as in laboratory analysis. Indeed, with a continuous bulk sample or a slurry, the irradiation and counting geometries can be in the range 1 to 4π and the effectively irradiated sample weight can be as much as several hundred grams. It has been found that the sensitivity, in terms of relative element concentration, can be an order of magnitude greater than in conventional small sample analysis.[3]

Radioisotope neutron sources have been found suitable for certain analyses, where both element concentration and neutron cross section are high.

Accelerator sources operated at an output of, say, 10^9 n/sec (only about 1% of maximum) are quite adequate for a range of analyses and have a much increased reliability and longer target life. An automatically controlled neutron generator is available[4] that maintains a constant flux by means of feedback circuitry and beam-sweeping techniques on a 3-in. by 3-in. target. The stability of the flux is within 2% (adequate for precise analysis, with the usual flux monitoring), and an output of 10^9 n/sec could be maintained for 75 hr, with good prospects for several hundred more hours' duration.

Detection Systems

The standard measurement system is a gamma-ray scintillation spectrometer using a 3-in.-diameter by 3-in.-thick NaI(Tl) crystal. This size has been found to be a suitable compromise between detection efficiency and cost and is now widely used. Larger crystals, in particular 5-in. diameter by 4-in. thick, are also in use.

For industrial conditions, thermal stability of the system gain is most important. Water cooling of the photomultiplier can be used; and the gamma-ray spectrum, if particularly simple, can be counted in toto, thus reducing considerably the need for gain control. The recent availability of ^{241}Am alpha sources embedded in the NaI(Tl) crystal has provided a convenient means for stabilizing the gamma-ray spectrum. The peak from ^{241}Am alpha particles appears at about 3 Mev on the gamma-ray energy scale, is sharp, and has no Compton distribution. A single channel analyzer window can be locked onto this peak to provide continuous automatic stabilization.

Annihilation radiation (511 kev) produced by positron-emitting radioisotopes can be detected by coincidence counting. This method is particularly effective in reducing background due to other radioactivity. The two photons from the β^+ decay are emitted in opposite directions, so it is only necessary to mount two detectors, one on each side of the sample.

Anticoincidence shielding has also been employed to reduce background in the detector in analysis by fast-neutron inelastic scattering. The method has been demonstrated for determination of carbon in coal.[4]

Ge(Li) detectors, with resolutions one to two orders of magnitude better than NaI(Tl), have not yet been used in industrial analyses. Their main disadvantage is the need for continuous cryogenic cooling, which is not at all impractical in an industrial environment since liquid nitrogen is now a very common commodity. The main application of Ge(Li) detectors will probably be in removing spectral interferences by resolving close gamma energies. For example, in ores containing both silicon and iron (a very common situation), the 1.77-Mev gamma ray from $^{28}Al[^{28}Si(n,p)^{28}Al]$ is completely resolved from the 1.81-Mev gamma ray from $^{56}Mn[^{56}Fe(n,p)^{56}Mn]$.

Applications

Batch Sample Analysis

Meinke and Shideler[5] in 1962 described a system using a commercially available neutron generator, with or without a moderator for thermal- or fast-neutron activation, respectively, which was suitable for routine analysis. At full power the thermal flux was 1×10^9 n/(cm^2)(sec) and the total fast-neutron output was 1.5×10^{11} n/sec. A rotating target was designed to present fresh areas to the beam and so prolong target life at maximum flux to over 20 hr. With intermittent irradiations, target life is extended to a few months. Samples were transferred remotely between generator and detector by means of a vacuum-operated pneumatic system.

Since then a number of other similar automated activation-analysis systems have been set up, but mainly for routine laboratory analysis.

Routine industrial activation analysis has been widely applied to determination of oxygen, particularly in steel. One method of activating oxygen is by the $^{16}O(n,p)^{16}N$ reaction using fast neutrons. Nitrogen-16 decays by emission of gamma rays with energies greater than 6 Mev and with a half-life of 7.4 sec. Steele and Meinke[6] reviewed earlier work on determination of oxygen by activation and reported analytical precisions of ±10% at the tens-of-ppm level. Anders and Briden[7] reported precisions of ±2% for the oxygen range 1 to 100% in a number of matrixes and sensitivities of well below 100 ppm. They recognized neutron-flux inhomogeneity as the main source of error and reduced this by spinning the sample during irradiation by using an air jet. Also, the need for uniformly packed powder samples was stressed. Mott and Orange[8] made a general study of precision and reported values as good as ±0.3%. They used a dual sample rotator for simultaneous irradiation of a sample and standard under highly reproducible geometrical conditions.

In 1963 a commercial fast-neutron activation-analysis system was installed in a steel works for routine oxygen determination.[9] Analytical results were generally within 10% of those obtained by vacuum fusion, inert-gas fusion, or chlorination techniques for oxygen contents from 5 to 500 ppm.

Although the neutron generators used in the above work were reported to be reliable and inexpensive to operate, the need to regularly change targets has been considered a disadvantage. Wood, Downton, and Bakes[10] reported the development and use of a sealed-tube neutron generator with a fast-neutron output of 10^{10} n/sec and a tube life of 100 hr at this output. The generator was housed in a 12-ft-deep hole in the ground, a convenient shielding method. Using the system, determinations were reported for oxygen in steel and O, Si, Al, Mg, and Fe in the NBS rock standards G1, W1, and R117.

Wood[11] recently reported the development and use of a system for the routine determination of nitrogen in food products (as a measure of the protein content). The instrument includes a sealed-tube neutron generator and pneumatic sample transfer system with provision for spinning the sample and standard about two axes. A schematic of the sample spinner is shown in Fig. 1. The standard serves as a neutron-flux monitor, and spinning both the sample and standard ensures identical and homogeneous irradiation conditions. The nuclear reaction used is $^{14}N(n,2n)^{13}N$; ^{13}N decays by positron emission with a half-life of 10.0 min. Reproducibility of the activation-analysis method was better than 1%, and agreement with the classical Kjeldahl method was excellent. Wood[12] has also recently reviewed activation analysis in the metals industry.

The measurement of silicon content of freshly cast iron[12] in an iron foundry is accomplished using a

33-curie ^{241}Am–Be source and automatic transfer system for a mold containing an 800-g sample. The nuclear reaction is ^{28}Si$(n,p)^{28}$Al; the product, with a half-life of 2.3 min, decays by emission of a 1.77-Mev gamma ray. The irradiation time used was 3 min and the counting time 2 min. Problems of airborne dust and high temperature in the environment of the foundry were overcome by enclosing the equipment and by refrigerating the scintillation-counter photomultiplier, respectively.

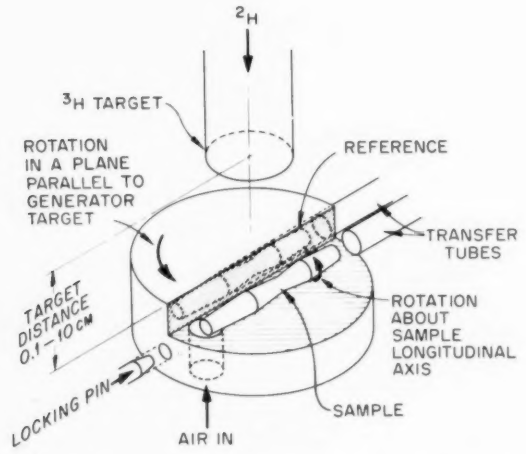

Fig. 1 Double-axis rotator. (Drawing by the courtesy of Kaman Nuclear Corp.)

Continuous Analysis of Liquids

On-stream neutron activation was demonstrated as early as 1962 by Anders,[13] who activated fluorine, silver, and selenium in aqueous solutions using a small ^{226}Ra–Be source (1.3×10^5 n/sec). The irradiation and counting cells each consisted of 90 ft of 0.5-in.-bore polyethylene tubing formed into 9-in.-diameter by 7-in.-long coils. Although counting rates were only 1 to 30 counts per channel per minute, necessitating irradiation and counting times of about 6 hr, the feasibility of rapid on-stream analysis using stronger sources was clearly demonstrated. However, the only radionuclides considered were 18 that had half-lives in the range 2 to 60 sec.

Gluck, McFarling, Kircher, Townley, and Sunderman[14] in 1961 studied on-stream production of intrinsic radiotracers for industrial process control. Although this is not the same as continuous-process analysis, the work is valuable for the design studies made on optimum cell volumes for irradiation and counting and on the functional relationships between flow rates, mean residence time in the irradiation cell, and mean delay time between irradiation and counting.

The irradiation cell was a cylindrical drum with an axial cavity for the source. The cell volume was 2.4 liters. Interior baffles were fitted to promote mixing and reduce streaming of the sample through the cell. The counting cell was of similar construction, surrounding a 2-in. by 2-in. NaI(Tl) crystal. The cell volume was 0.75 liter. Flow rates in the range 60 to 600 ml/min were used, depending mainly on the half-life of the radionuclide formed.

The sensitivities for determination of Mn, In, V, and Ag in aqueous solution were studied experimentally using 10- and 50-curie ^{210}Po–Be sources. Sensitivities for some 60 other elements were calculated and tabulated.

A facility for routine activation analysis of flowing solutions has been recently set up[3] and uses a pumped-tube neutron generator as the source, with a fast-neutron output of up to 2.5×10^{11} n/sec. Several 55-gal drums provide storage, and the liquids are transported in 1.5-in.-bore stainless-steel pipes. The irradiation cell is a cylinder positioned at the end of the neutron-generator drift tube (Fig. 2), equipped with baffles and having a volume of 5 liters. The counting cell is a similar cylinder with an axial reentrant portion enclosing a 3-in. by 3-in. NaI(Tl) crystal. Delay loops consisting of 100-ft-long coils of plastic tubing are incorporated into the analytical system when necessary.

One problem encountered with this system was significant activation of oxygen in the water, which caused interference even after a delay of up to 2 min. A prominent annihilation radiation peak was also found in the spectra from water due to pair production from ^{16}N gamma rays and positrons from the ^{14}N$(n,2n)^{13}$N and ^{16}O$(p,\alpha)^{13}$N reactions.

An interesting potential application studied was the measurement of sodium-to-phosphorus ratio in detergent materials. As a preliminary test a 20% aqueous solution of NaH_2PO_4 was pumped around the loop using a delay time of 30 sec. The ^{23}Na$(n,\alpha)^{20}$F reaction yields 1.63-Mev gamma rays from the 12-sec half-life ^{20}F. The ^{31}P$(n,\alpha)^{28}$Al reaction yields 1.77-Mev gamma rays from the 2.3-min half-life ^{28}Al. A spectrum stabilizer to prevent small drifts about the incompletely resolved gamma rays gives an overall precision of 0.63%, compared with 0.4% from the counting statistics. Since only the sodium-to-phosphorus ratio is required, neutron-flux monitoring

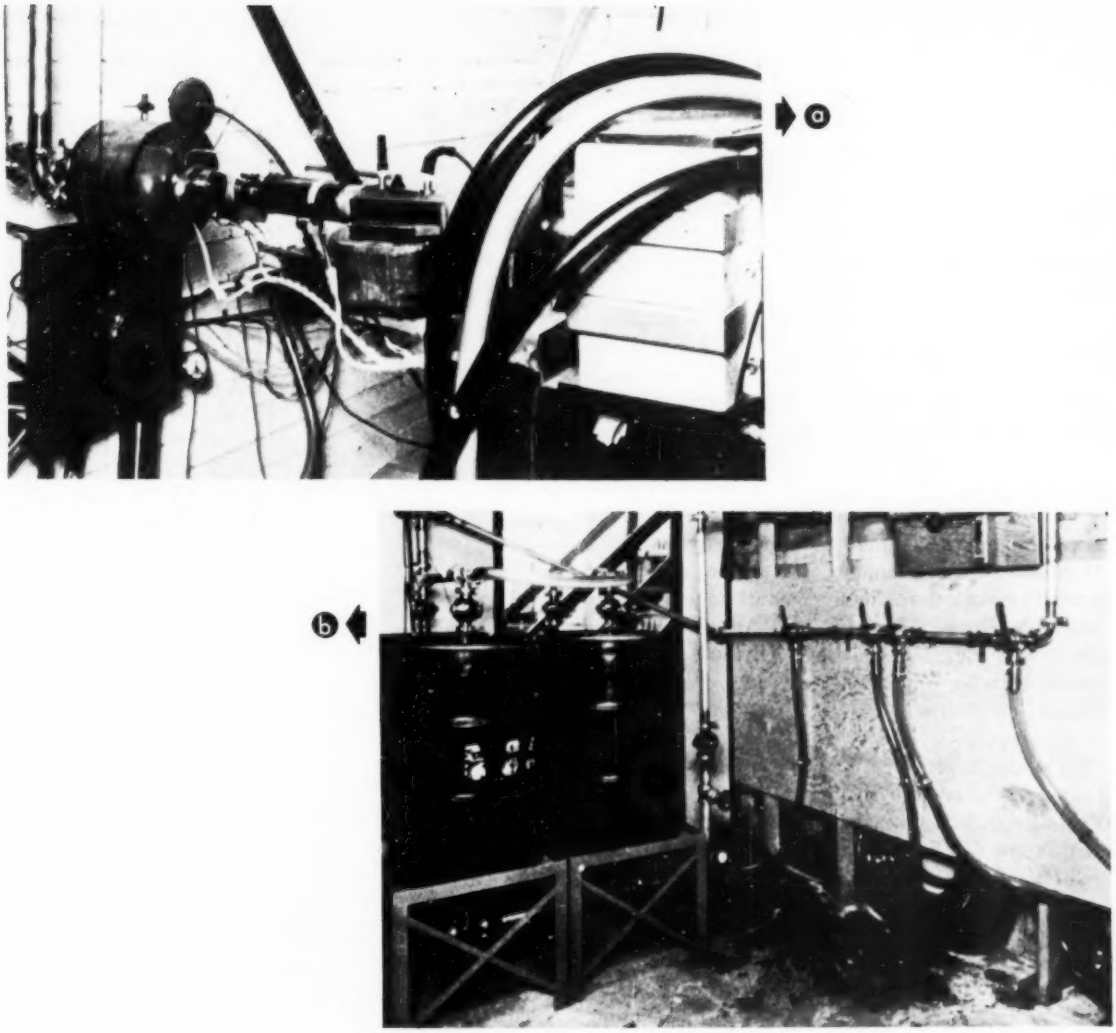

Fig. 2. Activation-analysis system for liquids showing (*a*) the irradiation station; (*b*) the sample holding, pumping, and delay facilities; and (*c*) the dismantled irradiation cell. (Photographs by the courtesy of Kaman Nuclear Corp.)

is not necessary. Although it was stated that control of the liquid flow rate to 0.1% would be required on account of the short half-life of ^{20}F, it should be possible to operate in a flow-rate range substantially independent of flow rate by using Gluck's[14] data.

Two investigators have set up loops designed primarily for analyzing ore slurries. Slurry transport imposes further constraints on the design of activation-analysis loops. Flow velocities of 3 to 10 ft/sec in connecting pipes are required to keep the slurry in suspension, and, under some conditions, it is necessary to continuously stir the slurry in the irradiation and counting cells. Thus reduction of the volume flow rate to increase the specific activity[3,4,13,14] is not always possible. Also, the use of long lengths of pipe for time delay may cause unacceptable increases in frictional losses and consequent head pressures.

Starnes (Hilger and Watts, Ltd., London) has set up a small slurry loop designed primarily for determination of fluorine and barium in fluorite–barytes slurries. Measurement of aluminum and silicon content of cement raw-mix slurries is also considered feasible. The source used is 3 curies of ^{241}Am–Be, and the detector, a 3-in. by 3-in. NaI(Tl) crystal. Reentrant, baffled cells for irradiation and counting, each with a volume of 3 liters, are connected by 0.5-in.-bore plastics tubing.

Fluorine is activated by the $^{19}F(n,\alpha)^{16}N$ reaction (gamma-ray energies over 6 Mev, half-life 7.4 sec). An advantage of using the radioisotope source is that its neutron energy is too low to activate oxygen. Barium is activated by the $^{138}Ba(n,2n)^{137m}Ba$ reaction (gamma-ray energy 0.66 Mev, half-life 2.6 min).

A unique recirculating system is used to provide stability in the analysis loop during measurement. With flow in one direction, the delay between irradiation and counting is about 4 sec, which allows the fluorine determination to be made. With the flow reversed, the delay is about 50 sec, allowing the ^{16}N activity to decay and the barium determination to be made.

The solids content of the slurry (about 35 wt.%) is monitored continuously with a ^{137}Cs gamma-ray density gage. Figure 3 shows a calibration curve obtained using various fluorite ores at different solids contents.

The Texas Nuclear slurry loop[15] is a nonrecirculating system with 1100-gal holding tanks; a 10-gal (max. volume) stirred, reentrant irradiation cell; and either 0.75- or 0.5-in.-diameter interconnecting plastic tubing. Figure 4 is a schematic of the system. The delay cell can be replaced by a length or coil of tubing if conditions permit. Although the cells are shown with

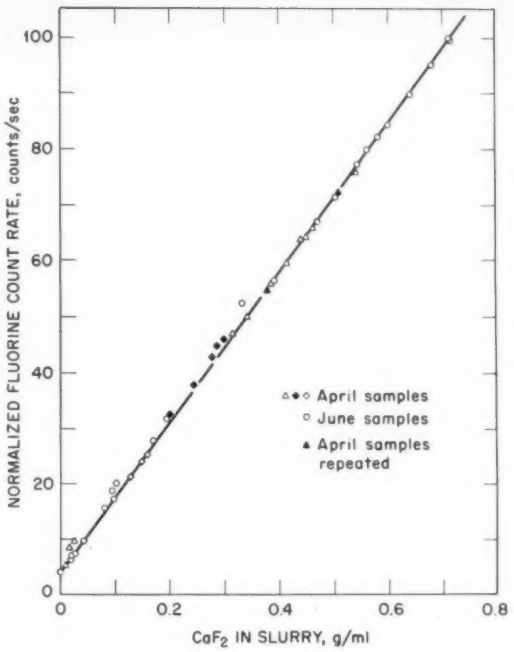

Fig. 3 Plot of ^{16}N gamma-ray count rate vs. volume concentration of calcium fluoride in fluorite ore slurries. (Drawing by the courtesy of Hilger and Watts, Ltd.)

stirrers, experiments with unstirred, baffled tanks are in progress. The neutron source is a standard pumped-tube neutron generator with automatic flux control via a proton-recoil telescope flux monitor.[4] Although the generator used has a maximum output of 4×10^{11} n/sec, outputs of only 10^9 n/sec are necessary for the determinations studied, resulting in an expected increase in target life by two orders of magnitude. The detector is a 3-in. by 3-in. NaI(Tl) crystal.

Preliminary trials showed that the background due to ^{16}N activity in the water was negligible with delay times of about 1 min. Recirculation of the sample allowed significant and undesirable buildup of longer-lived activity (e.g., iron).

An important problem in the iron-ore processing industry is the monitoring of the silica content during production of iron concentrate from taconite ores. The concentrate contains 5 to 10% SiO_2 and 60 to 65% iron. Figure 5 shows a gamma-ray spectrum obtained during continuous monitoring of Atlantic City taconite concentrate. The solids content of the slurry was 20 wt.%, and these solids contained 11.6% SiO_2 and 62.5% Fe. The slurry flow rate was 8 gal/min, the bore

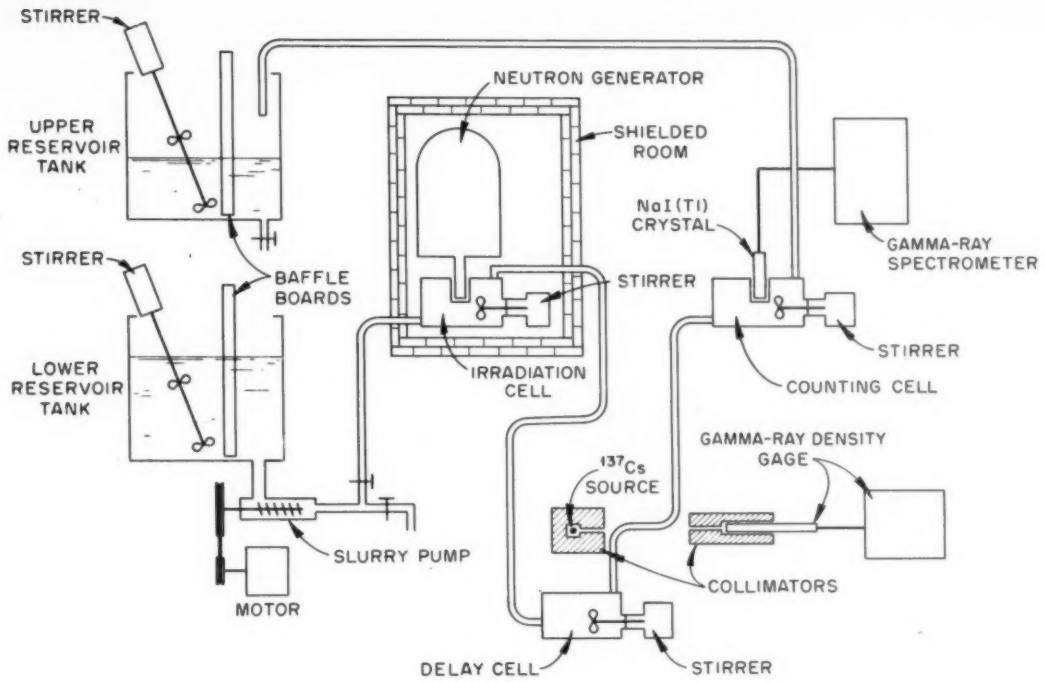

Fig. 4 Schematic layout of slurry loop.

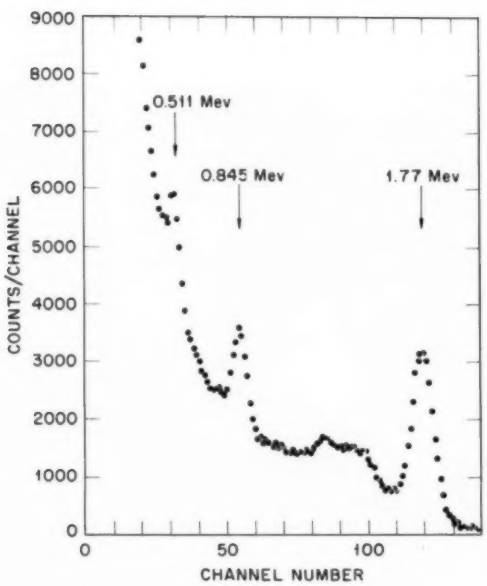

Fig. 5 Spectrum from Atlantic City ore during continuous flow as aqueous slurry (counting time 2 min).

of the interconnecting pipes was 0.75 in., and the counting time was 2 min. The 1.77-Mev peak from 2.3-min $^{28}Al[^{28}Si(n,p)^{28}Al]$ and the 0.845-Mev peak from 2.6-hr $^{56}Mn[^{56}Fe(n,p)^{56}Mn]$ are prominent. The neutron output was about 10^9 n/sec.

Rapid on-stream determination of silicon content is clearly feasible.

Continuous Analysis of Bulk Solids

A pilot-plant facility for continuous analysis of bulk materials has been set up at Texas Nuclear Corporation in conjunction with the USAEC.[4,15,16] The materials-handling system included a 25-ton storage hopper, a 2-ton feed hopper, a forced-feed screw conveyor, and analysis and discharge conveyor belts. Material can be continuously fed under a leveling bar onto the analysis belt, which is a standard 18-in.-wide conveyor that can be moved at speeds from 2 to 50 ft/min. The pumped-tube-type neutron generator is automatically controlled and completely enclosed in a dustproof and flameproof cylinder. Two detectors are available: one collimated, shielded, and aimed at the irradiation point; the second, shielded and some 15 ft

downstream of the neutron generator. The former is used to detect prompt gamma rays, and the latter, decay gamma rays from the activated material.

Previous studies reported using this system included determination of C, O, Al, and Si in coal.[4,17] Gray and Metcalf[9] have also studied on-stream activation for determination of aluminum, silicon, and iron in coal using a similar facility. Other investigations using the Texas Nuclear system have been on the measurement of aluminum and silicon in bauxite and cement raw mix and of silicon and iron in taconite.[15] Figure 6 is a photograph of the irradiation head, with

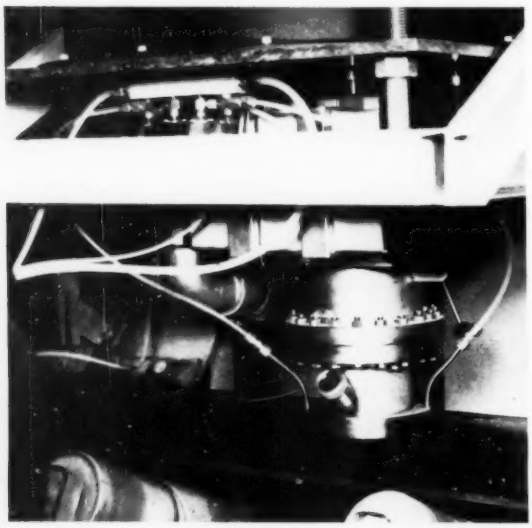

Fig. 6 Bulk-solids facility irradiation head with coal on the analysis belt.

coal on the analysis belt. Figure 7 shows a calibration obtained during runs of three different taconite ores. For each run some 2 tons of ore were fed continuously through the system. Each run lasted about an hour, irradiation was continuous, and 2-min counts of the ^{56}Mn and ^{28}Al gamma-ray peaks were taken every 2 min. With a belt speed of 10 ft/min, the delay between activation and counting was ~1.5 min. The spectra obtained were similar to that shown in Fig. 5 for taconite slurries.

Recent work on copper ores[15] in a joint operation between Texas Nuclear, the USAEC, and industry has resulted in an activation-analysis facility being set up at a copper-ore-processing pilot plant. The input to the ball mill, which consists of coarse ore (~¼ in.), is fed

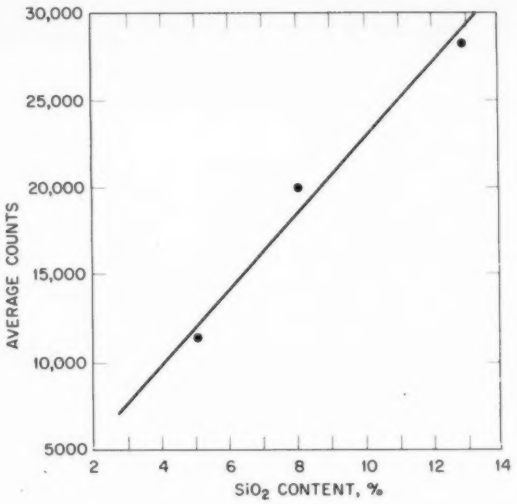

Fig. 7 Plot of count rate of ^{28}Al gamma rays vs. silica content of taconite ore concentrates, taken during continuous runs of three different ores (counting time 2 min).

by conveyor belt under an automated neutron generator and then out of the shielded enclosure and under a gamma-ray spectrometer. A photograph of part of the installation is shown in Fig. 8. On the right is the shielded enclosure housing the neutron generator. Irradiated ore is seen passing under the measuring head.

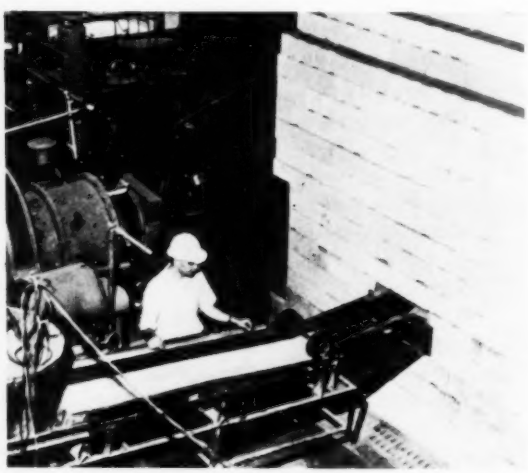

Fig. 8 Activation-analysis installation at a copper-ore-processing pilot plant: The irradiated ore is shown passing under the gamma-ray spectrometer. (Photograph by the courtesy of Kennecott Copper Corp.)

Copper is activated by the $^{63}Cu(n,2n)^{62}Cu$ reaction, the product being a positron emitter of 9.7-min half-life. Silicon is also activated strongly, and a delay of at least 15 min, to allow decay of the 2.3-min ^{28}Al product, is required to permit the 0.511-Mev annihilation radiation from ^{62}Cu to be counted in the presence of the ^{28}Al Compton background using gamma-ray spectrometry. The use of coincidence counting, however, enables this background to be almost entirely eliminated. Preliminary results have been obtained at the pilot plant with NaI(Tl) detectors above and below the conveyor belt. Figure 9 shows a calibration ob-

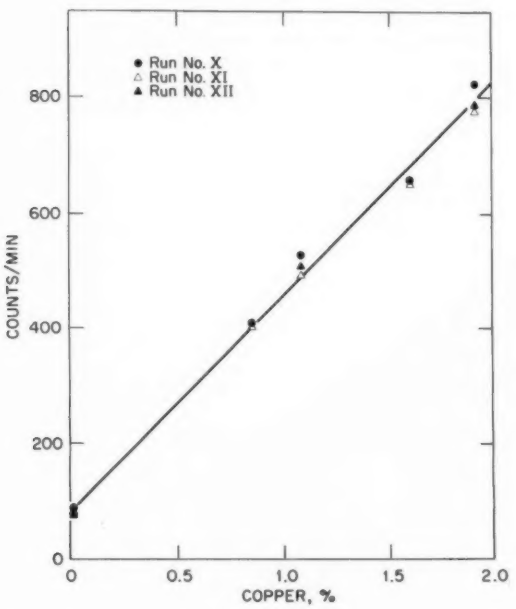

Fig. 9 Percent copper vs. counts per minute for runs X, XI, and XII, indicating reproducibility of copper data.

tained during continuous measurement of a number of natural and "salted" copper ores. It should be emphasized that no sample preparation was required. The coarse ore with its top surface scraped flat was presented on an ordinary conveyor belt.

Discussion

Although only preliminary results have been obtained so far, it is quite clear that neutron activation is an ideal method for on-stream analysis of bulk solids and ore slurries in industrial conditions. The lack of matrix and heterogeneity effects represents a significant advance in this form of analysis.

At this early stage in the development of the technique, a number of problems are evident. The optimum neutron source for a given analysis is not yet known, whether it be radioisotope, pumped-tube neutron generator, or sealed-tube neutron generator. Design of equipment for ensuring constant presentation geometry of bulk solids is rudimentary, and the optimum sizes of cells for fluid analysis are not known. The need to enclose the neutron generator in a concrete blockhouse for personnel shielding is a fact that one would hope industrialists will accept.

It is probable that neutron activation will be complementary to X-ray fluorescence, which, at present, is one of the most widely used on-stream analysis techniques for solids, liquids, and slurries. Many of the elements most easily measured by activation analysis (e.g., O, N, F, Na, Al, Si, and P) are light elements, important in industrial processes and almost impossible to determine by X-ray fluorescence. On the other hand, most heavier elements can be determined by X-ray fluorescence, with increasing freedom from heterogeneity effects at higher atomic numbers. An industrial analysis in which the two systems would complement each other beautifully is on-stream determination of Al, Si, Ca, and Fe in cement raw mix. Calcium must be determined by X-ray fluorescence, which can also be used for iron. Aluminum and silicon are ideally suited for determination by neutron activation.

Acknowledgments

The author is grateful for the stimulation, encouragement, and advice given by Ira Lon Morgan, who suggested this paper, and to John B. Ashe for many interesting and penetrating discussions. The ready supply of data and experimental results by Peter E. Starnes (Hilger and Watts, Ltd.) and Don E. Wood (Kaman Nuclear Corporation) is also gratefully acknowledged. (RHL)

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Extended Testing of the Methane Ionization Detector

By Joel R. Finkel* and Philip J. McCabe†

Abstract: *The development, construction, and performance of an instrument for the detection of methane during coal mining operations are described. The equipment can be directly attached to the coal-digging machine and is capable of withstanding the abuse and hostile conditions associated with the mining process: high humidity, violent vibrations, and large voltage surges. Two alarm levels are provided for triggering at concentrations of either 1 or 2% methane. Details of the tritium detector cells, electronics, and mechanical construction are presented.*

In the past 130 years, the undetected presence of methane in the atmosphere of coal mines was found to be the cause of about 470 subterranean explosions in which almost 11 thousand lives were lost. The only way to prevent these occurrences is to monitor the buildup of methane-gas concentrations so that preventive measures may be instituted before it reaches the lower (~5.3% CH_4 v/v) explosive limit. Most of the presently available devices that can detect methane must be operated by skilled technical personnel under relatively placid conditions that are not realistic insofar as immediate detection capability in the rigorous mine environment is concerned. Those devices which are amenable to operation in coal mines require frequent, or continuous, operator attention and frequent maintenance. They often give false positive indications of excessive methane concentration causing unnecessary shutdowns of the mining operations. The ideal detector should have good selectivity and high sensitivity, low noise level and drift rate, and simple operational and maintenance requirements. It should also be unaffected by moisture or coal dust, be capable of fully automatic operation, and should not be inherently capable of

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initiating an explosion during either normal or defective operation. The Methane Ionization Detector described herein meets all these requirements.

In 1963 Melpar, Inc., developed and successfully tested (with corporate funds) a cross-section ionization detection system that was sensitive to several gases, including methane. Fully aware that this system was useful as a methane sensor in coal mines, but not cognizant of all conditions that might be encountered in an operating mine, Melpar approached the U. S. Bureau of Mines about sponsoring a program to determine how the Melpar Methane Detector might best be packaged for use in the rigorous environment of a coal mine, under typical operating conditions where possible, i.e., power available, surge power on line, vibration, and the like. As a result, a contract was entered into [Contract AT(30-1)-3298] for the purpose of developing a suitable packaging arrangement. A separate contract [AT(30-1)-3717], the present one, involved extended testing of the Melpar Methane Ionization Detector and making such modifications of the unit as were found necessary for trouble-free operation of the detector within an actual operating mine. This work, under the second contract, has now been completed, and the results of the program are described in this report.

Essentially the packaged methane detector consists of a gas transport system, two cross-section ionization detectors, an amplifier and other electronics, and a warning indicator. These component sections will be discussed separately. The entire unit is housed in a U. S. Bureau of Mines-approved, explosion-proof case with approved electrical connectors. The unit is shown in Fig. 1. The control panel consists of an on/off lamp

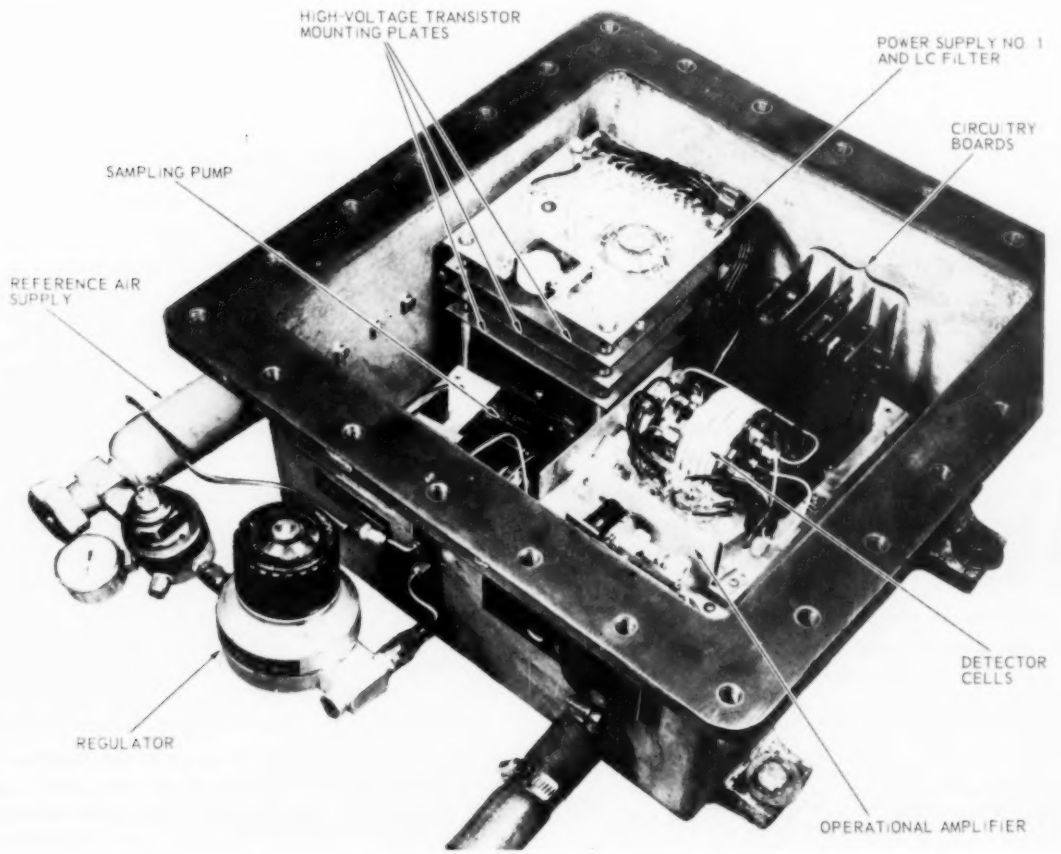

Fig. 1 Methane Ionization Detector.

test switch and two signal lights set to respond to 1 and 2% methane-concentration levels, respectively.

Results and Discussions

Theory of Operation

The principle of operation of the Melpar unit is quite simple. It utilizes a cross-section ionization detector as the basic transducer. Each cell of the transducer consists of two parallel foil electrodes; each foil electrode contains 1 curie of titanium tritide. One of the foils is connected to a d-c power supply, while the other electrode is connected to a d-c amplifier. The current, I, of an ionization detector having a fixed internal volume, V, can be expressed as

$$I = k\left(\frac{PV}{RT}\right)XQ$$

where P, R, and T = pressure, gas constant, and temperature, respectively
k = proportionality constant
X = molar fraction of gas being ionized
Q = ionization cross section for this gas

Thus this transducer will produce a change in output current whenever the gas composition, temperature, or pressure is varied. In normal coal mines, only the concentration of methane and water in the air will vary drastically.* Fortunately this transducer is extremely insensitive to water vapor (but not to condensed water within the detector spacing) so that only changes in the methane concentration will be sensed.

Since it is essential that the detector unit be operated at an applied potential sufficient to collect all the ions generated within the cell spacing, current vs. applied voltage curves were run for both sides of the detector. The experimental arrangement and the curve of the results are shown in Fig. 2. On the basis of the results of this experiment, the applied potential across the detector was adjusted to approximately 85 volts to provide sufficient potential to collect all the ions generated and to be able to overcome the space charge that would be generated within the relatively large cell volume. A calibration curve of detector signal, in volts, vs. concentration of methane, in percent methane in clean air, was run to determine the degree of linearity of the system. It was found that the response was

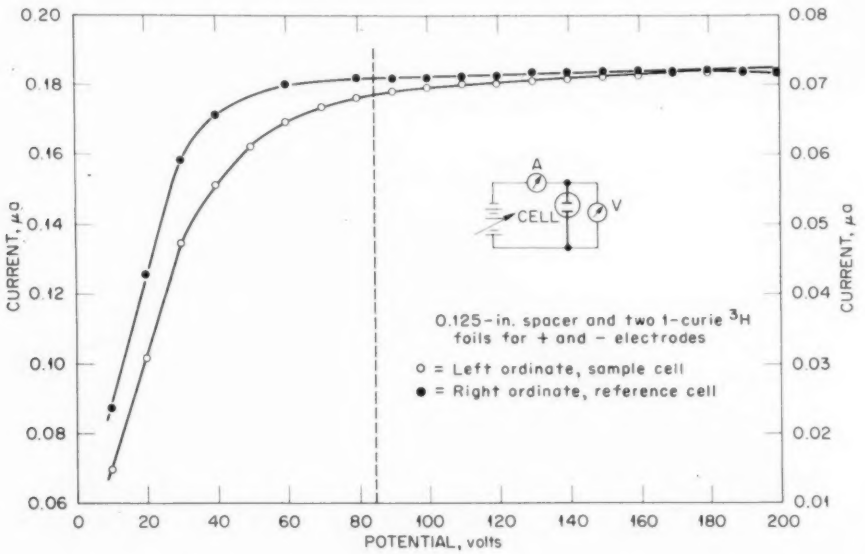

Fig. 2 Current–voltage relation for clean air as established by β^- ionization cell.

*The concentration of carbon dioxide must increase more than fivefold before any false signal would occur; concentration of carbon monoxide would have to rise well above the lethal concentration before any false signal occurs. Hence neither gas will tend to interfere with the proper operation of the methane detector.

perfectly linear for concentrations of up to 3% methane in air, and that for concentrations between 3 and 10% methane the cell became progressively more nonlinear. At concentrations >10%, the cell became saturated and there was no further change. Figure 3 shows this change in signal level with change in methane concentration.

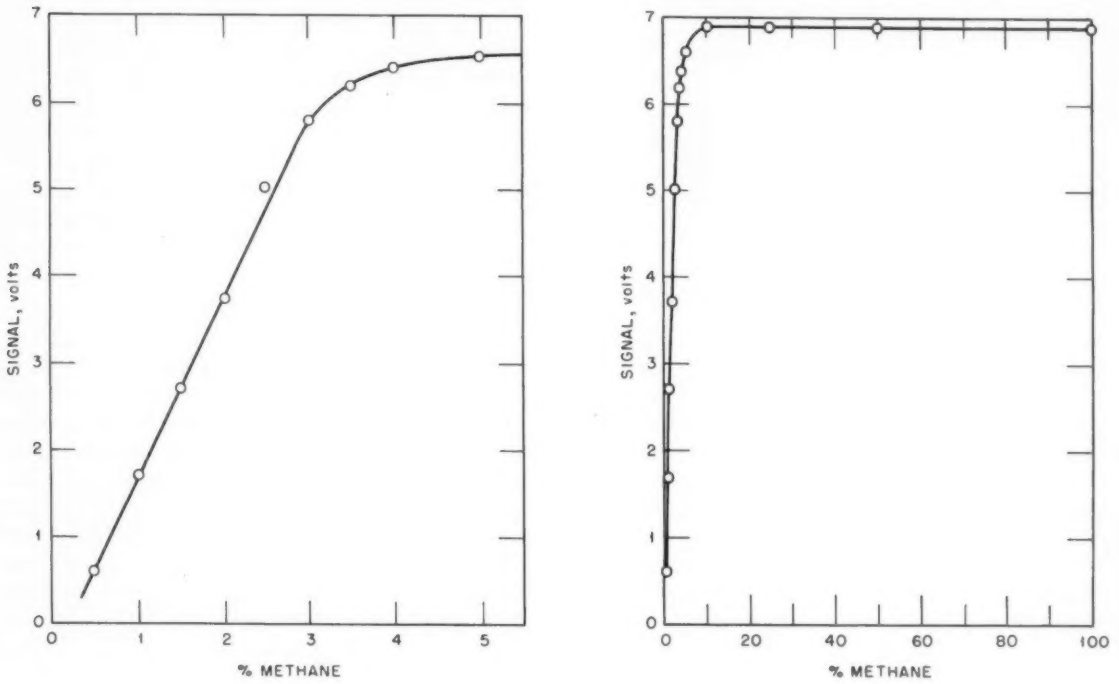

Fig. 3 Response of detector to % methane.

Gas Transport System

A major problem with the first probe was its tendency to become clogged with coal dust after only a few minutes of operation. Therefore a baffled probe housing was fabricated to prevent excessive accumulation of coal dust on the probe. This probe housing was tested under simulated dust conditions in the Melpar laboratories, utilizing 10-μ MMD acetylene black at a concentration level in excess of 50 million particles per cubic yard, and no acetylene black was observed to have been deposited on the probe. Accordingly the device was tested for 48 hr in a mine. Figure 4 shows the probe housing and the probe after this test period. The accumulation of coal dust on the outside surface of the probe housing is readily apparent; however, it can be seen that there was no accumulation of coal dust on the probe. Nevertheless, it should be noted that the environment associated with the coal-mining operation is much more hostile than initially anticipated. There is a continuous problem with large chunks (as much as 100 lb) of coal falling from the roof as the overlying strata undergo stress relief subsequent to excavation of the seam. While these chunks will not damage the detector housing, they could conceivably damage the probe or the probe line.

The overall gas transport system is shown in Fig. 5. The compressed-air bottle provides a reference level for the detector which improves the unit's ability to detect very slow, small changes in methane concentration. The reference air is sampled for approximately 8 sec of each 30-sec cycle. At this sampling rate a standard lecture bottle of compressed air (containing 2 cu ft at 1800 psi) provides sufficient reference gas for more than three full work shifts. For easy access the bottle is located on the outside of the explosion-proof case. A thermostatically controlled heater circuit was added to

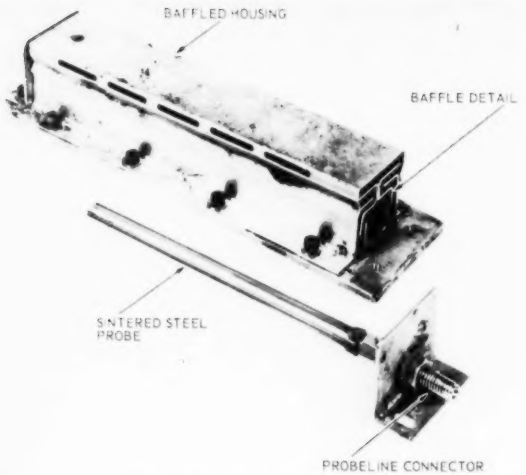

Fig. 4 Sample probe and housing.

the detector housing to prevent condensation of water vapor inside the detector.

Early in the course of the laboratory evaluation, pneumatic oscillations were observed that arose from the pneumatic tank circuit, much in the same manner as oscillations occur in an *RC* electronic circuit. Thus it was necessary to expend considerable effort in balancing the pneumatic loads of the gas transport system. When this was achieved (i.e., elimination of the oscillations by balancing), both the accuracy and repeatability of the detector were improved.

Electronics

The electronics portion of the methane detector consists of three basic sections: the power supply, the detector/amplifier, and the alarm circuits. The power supply can be further subdivided into separate functional units: surge regulator, converter, series regulator, and secondary power supply. A block diagram of the circuit schematic is shown in Fig. 6. Shortly after the work on this program was initiated, Melpar was informed by the Bureau of Mines that they were no longer interested in providing capabilities for both self-contained power supply and mine power operation of the unit and were only interested in using mine power sources. This permitted a great simplification in the complexity of the circuitry for the methane detector by eliminating all the battery-charging circuitry, including the relays that had been a source of trouble in the past.

The power supply converts the mine power, nominally 250 ± 125 volts, to the several voltages required by the individual components of the unit. Since the input voltage from the mine can vary between the previously mentioned 125 to 375 volts direct current, and pulses, or instantaneous surges, well in excess of 1000 to 3000 volts have been observed on these power sources, the power supply had to be very rugged. These surges, apparently, were the cause of a "burnout" of a custom-fabricated transformer in the converter (during the period of the previous contract). This unit (i.e., the transformer) was replaced with one

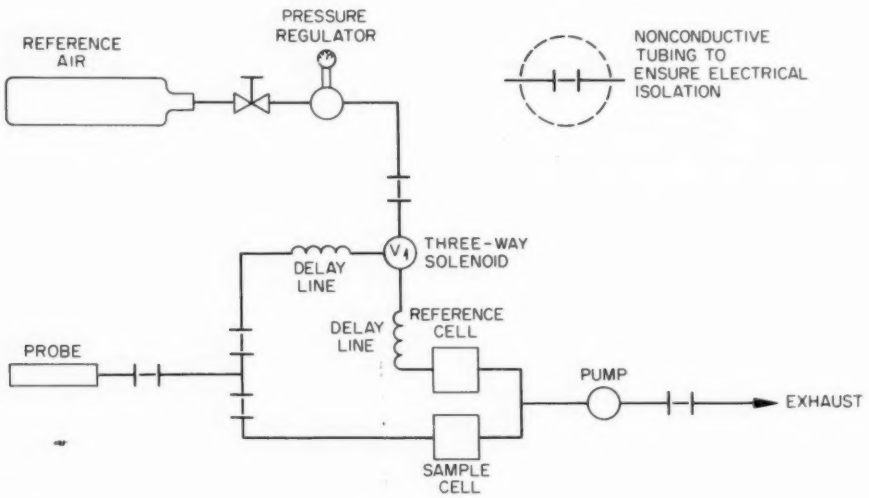

Fig. 5 Gas transport system.

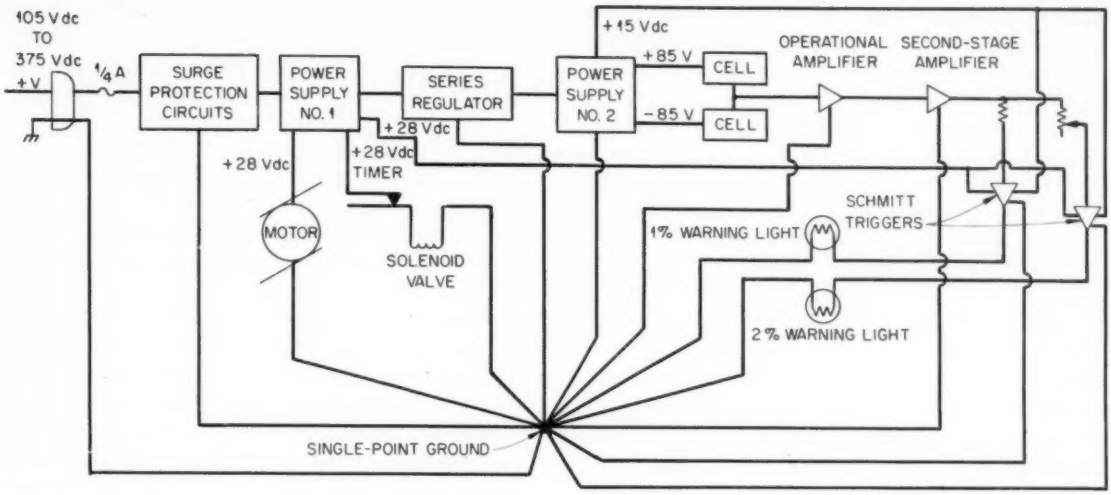

Fig. 6 Electronics block diagram.

of larger power rating, and additional surge protection was added to the circuitry. The circuit is protected by a ¼-amp fuse capable of withstanding the high voltages; the fuse has a very high instantaneous current rating consistent with the surges known to occur in the mine power source. The surge suppressor is a gas-discharge device that grounds all surges greater than 600 volts. In addition, there is an inductance/capacitance filter to eliminate short-duration pulses ranging from 350 to approximately 700 volts, and a back-to-back zener diode device to shunt these surges.

The "desurged" voltage is now connected to a transformer-coupled multivibrator and a series regulator. The multivibrator precedes the series regulator that is connected to ground so as to make best use of the available transistor polarities. The transistors used in these circuits are high-power, high-voltage units. The multivibrator is a standard circuit, and the series regulator is nearly standard, except that its output is a function of the multivibrator output. The series regulator is also a circuit protective device that will disconnect when an overload surge arises. This disconnect is accomplished using a silicon-controlled rectifier; the instrument may be reset by momentary removal of power.

The secondary of the multivibrator produces 28 volts after rectification and filtering. This voltage operates the pump motor, the solenoid valve, and the signal lamps, in addition to a second multivibrator power supply. The second power supply produces the positive and negative 85 volts used for polarizing the detector and the positive and negative 15 volts utilized for the Schmitt triggers and the operational amplifier. A Philbrick P2A amplifier was chosen because of its very high input impedance that matches the high impedances of the detector and reference cells. It is essential that current drain from the system be minimized. Finally, the amplifier was a-c coupled to the detector to eliminate long-term drift problems.

The detectors are arranged in series between the positive and negative 85-volt power supplies so that the voltage at the junction of the two is at ground potential when the two cells are filled with gas of the same composition. For different compositions the voltage drop across the cells will not be the same and the potential at the junction between the two will deviate from ground. This junction potential is the signal of interest. It is loaded with a very high impedance (100 megohms) coupled through a capacitor that is differentiated by another very high level resistor and then led to the noninverting input of the amplifier. The inverting input of the amplifier is used to provide gain control and stability. The output of the amplifier goes to the Schmitt-trigger level sensors that are set to alarm at predetermined methane levels. The amplifier is connected through an emitter–follower circuit within the feedback loop of the amplifier.

The equipment is normally set to alarm on 1 and 2% methane concentrations. The output of the amplifier is connected directly to a Schmitt trigger that is the 1% level detector (calibrated by adjustment of the gain potentiometer of the amplifier circuit). The 2%

alarm is a similar circuit, but its input is through a potentiometer. This potentiometer is used to adjust the 2% alarm level. The output of the Schmitt trigger is then connected through a protective resistor to a remote recorder output circuit that is used in calibration and setup of the system. In the commercial device this last output would be utilized to control the power interrupters to a mining machine.

Mine Testing and Corrective Action

During the course of the first series of mine tests, difficulty was encountered with ground loops and with leaks to ground and short circuits caused by high humidity. Another difficulty occurred when, after a period of operation under conditions of very high relative humidity (greater than 90%) followed by shutdown and storage under cold conditions, water vapor condensed on the inside of the detector cell. While water vapor, per se, will not affect the operation of the detector, the presence of liquid water within the detector will cause cell-shorting problems. When this condition developed, it was necessary to remove the unit from the mine to dry it out.

During this above-ground drying-out process, a combination of reversed connector polarities and ground-loop difficulties led to the inadvertent drawing of an arc between the readout circuitry and ground. This arc completely destroyed the readout circuitry and substantially damaged the series regulator and power supplies.

Upon return to Melpar a complete "postmortem" of the methane detector electronics was carried out. As a result of this postmortem examination, the circuitry was rearranged on small printed circuit boards. This was done to avoid the ground-loop problems that led to the short-circuiting damage. Each of the printed circuit boards had its own separate ground circuit. These separate ground circuits were, in turn, connected to a single-point ground terminal within the instrument; this terminal was then connected to electrical ground. A chassis ground connection was run from all electrically isolated or pneumatic portions of the unit to another ground terminal that was separate from the single-point ground. This second ground was then connected with earth.

At the time of the postmortem examination, it was noted that much of the problem was apparently due to condensation of water on the metal mounting plate. (This metal plate was initially used to mount the electrical components so as to afford stability and rigidity to the unit during the course of the rather vigorous vibration anticipated when the instrument was mounted on a mining machine.) This finding resulted in a changeover to nonconductive circuit boards and to the complete coating of all the parts with Glyptal, with the exception of surfaces in the immediate vicinity of adjustable elements (e.g., potentiometers). In addition, the Delco power resistors, which dissipate a rather large quantity of heat, and the inductors and specially wound transformers were mounted individually on 6- by 6-in. aluminum plates to provide an adequate heat sink.

Upon completion of the rearrangement and the waterproofing, the instrument was assembled and exposed to a steam generator just prior to bolting down the lid to assure a very high humidity content inside the unit. It was then moved into a refrigerated test chamber and rapidly cooled to a temperature of approximately 50°F. Proper operation was observed when the unit was activated after a 2-hr soaking period. This procedure of steam injection followed by rapid cooling and soaking for various periods was repeated several more times. After each cycle the unit functioned without difficulty, thus indicating that moisture condensation would no longer be a problem.

During the course of the corrective action, ground-loop problems caused by the detector's high input impedance and current levels were detected. These were remedied by relocating the P2A operational amplifier within the detector compartment. All connections in and out of the detector compartment were made with a special low-loss coax cable. The coax shields were connected to a single ground point.

In addition to the corrective action already described, additional electromagnetic-interference shielding was placed around electronic noise-generating components, such as the Brailsford pump motor. Electronic isolation of the instrument from the case and the surrounding environment was achieved by the use of Teflon or Zytel tube fittings inside the explosion-proof housing so that there would be no direct electrical path through the gas tubing to the outside. Wiring was rearranged so as to minimize electrostatic pickup and cross talk. An improved surge protector from Dale Electronics, Inc., was added to the system. This device is capable of interrupting all surges between 600 and approximately 4000 volts direct current.* In addition, the type 8 AG fast-acting instrument fuse was

*Bureau of Mines personnel have frequently measured voltage spikes or surges of 2500 to 3500 volts direct current in a (nominally) 250-volt d-c mine power line (E. Coggeshall, U. S. Bureau of Mines, Pittsburgh, personal communication).

replaced by a type 3 AB steatite-enclosed arc-quenching, powder-filled fuse to minimize arc carry-over across a blown fuse. Moreover, this type of fuse should be much less sensitive to failure arising from mechanical vibrations than the previously employed instrument fuse.

The unit was set up in the Bureau of Mines laboratory in Pittsburgh to calibrate trigger levels and to serve as a preliminary demonstration for the Bureau's personnel. Natural gas (containing approximately 2 to 4% ethane impurity) was used instead of pure methane. Various concentrations of gas in air, ranging from 0.5 to 2.5%, were introduced into a test gallery containing the sample probe. The response of the unit was compared to a Riken optically indicating methane detector; the readings obtained on the two devices agreed throughout the course of the laboratory demonstration. Repeatability and reliability of the unit were demonstrated, with the 1 and/or 2% indication lights triggering only when the gas concentrations exceeded these levels.

At the end of the first day of testing in the Bruceton facility, all power to the instrument was shut off and it was left in the mine overnight. After normal warm-up the following morning, the instrument functioned without difficulty, faithfully following the repeated cycling of the gas concentrations. Additionally, the accuracy of the methane detector was compared with that of the Riken instrument and there was no disagreement between the two.

Subsequently, the detector was taken to the Clyde mine of the Republic Steel Corporation near Fredericktown, Pa. The plug fittings and external screws located on the explosion-proof housing were spot-welded to ensure that they would not come loose or fall out as a result of vibration while mounted on the mining machine, since the detector was later to be installed on a Joy Manufacturing Company (Model 1CM) continuous mining machine located in an area of the mine where a methane ignition had taken place a week before this testing (if gas were to be found at any point in the mine, this would be the most likely spot). Unfortunately the spot welding caused a terminal board to warp slightly, which created a short circuit in the power circuitry; this was easily corrected.

A great deal of difficulty was encountered in finding a suitable spot on the mining machine on which to mount the sampling probe. In ordinary operation the digging head moves in three directions simultaneously (forward and backward—approximately 30 in.; side to side—approximately 15 ft; up and down—approximately 8 ft). These articulations of the digging head cause undesirable flexing of the stainless-steel tubing presently utilized in the sampling line. Furthermore, the commonly employed types of continuous mining machine have roof jacks and boring tools mounted on them so that ceiling crossbeams and roof drill plates can be inserted by the same machine that does the digging of the coal. Either can very easily pinch off the gas conduit if it is not properly located. These difficulties can be ameliorated by the use of flexible armored hose instead of stainless-steel tubing. Since there were no suitable fastening points at the front of the digging head, the probe was mounted just behind the digging head. Although this was not the closest point to the coal face, it was close enough to detect any release of pockets of methane gas.

The methane detector was operated for three shifts per day for 2 days. No difficulties were encountered during this 48-hr period of continuous operation other than a fuse failure that was traced to a mechanical imperfection in the fuse wire.

Although, according to resident miners, most methane monitors tend to give false positive indications of methane, the Melpar Methane Ionization Detector gave none during the course of this rigorous test period.

(DNH)

Radioisotopes and Oceanography

By G. H. Keller*

Abstract: *A brief review of the literature indicates that, although radioisotope methodology in oceanography is not yet extensive, significant developments have been made. Radioisotope methods have been used for making observations directly in the environment and for tagging and dating both water masses and sediments. Only prototype nuclear instruments have been, in general, used thus far, but results obtained with them indicate the feasibility of using such instruments for measuring current velocity, oxygen content, deposited-sediment density, suspended-sediment concentration, and the elemental compositions of bottom sediments.*

Although oceans cover approximately 70% of the earth's surface, we understand very little about the processes taking place in this dynamic environment. Relatively little is known about the physical and chemical characteristics of the oceans or the processes responsible for shaping the ocean basins. Numerous investigations have been conducted in this environment, but its vastness plus the great expense per unit of data have left us far from adequately describing it. Technical advances in recent years, particularly computers and electronic sensors, have enabled the oceanographer to collect and process large amounts of information. Of particular significance are breakthroughs in the area of in-place measurements, which have provided the investigator with data of far greater accuracy and significance than have been obtained in the past.

Radioisotopes have recently become important in oceanographic and coastal engineering research. Both natural and artificial radioisotopes are used not only to trace and date water masses and to study their chemical characteristics but also to provide an entirely new field of instrumentation ideally suited to the in-place measurements of various properties of the ocean and the underlying sea floor. Some of these applications are summarized below.

Radioisotope Tracers

Radioisotope tracers used in oceanographic measurements may be those of natural origin—radioisotopes and their daughters present since the earth's formation or those produced by the interaction of cosmic rays with elements in the earth's atmosphere—or those produced artificially as by-products of nuclear explosions or atomic waste.

Naturally Occurring Radioisotopes

Radioisotopes, with their unique parent–daughter relationships, have provided the scientist with an excellent tracer as well as an age-dating method. For example, studies of the disequilibrium of ^{234}Th in the ocean have shown that in some areas of the sea the isotope has been removed from the surface waters and concentrated at the thermocline, i.e., the zone where the temperature gradient is greatest. Similar studies using ^{32}Si have enabled the oceanographer to date and trace the movement of specific water masses. Results of studies of the depth distribution of ^{234}Th show promise of providing an insight into the mechanism by which trace elements are removed from certain portions of the water column; this, in turn, could lead to a better understanding of the settling rate of variously sized particles through the water.[1]

The short residence time of thorium in seawater (35 ± 35 years) and the assumption that the isotopes ^{232}Th and ^{230}Th are precipitated in the same ratio permit determination of the accumulation rates of such elements as Mn, Ni, Co, and Cu in deep-sea deposits.[2] By measuring the activity of ^{26}Al, which is present in submarine sediments, the geological oceanographer has developed a suitable technique for calculating the rate at which the sea floor is receiving sediment particles.[3] Such observations are vital to an understanding of the depositional history of sea-floor deposits.

The disequilibrium technique of age dating has developed rapidly in recent years, and several isotopes (^{32}Si, ^{234}U, ^{231}Pa, and ^{14}C) are now used to provide absolute age determinations of rocks and shells found in the ocean basins.[4-6] These data have made it possible for scientists to define, with increasing accuracy, the time and mode of formation of the ocean basin as well as to determine the various stands of the sea through geologic time.[7]

Artificially Produced Radioisotopes

Radioisotopes added to the oceanic environment as a result of fallout from nuclear weapons, nuclear power

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plants, and disposal of atomic wastes in ocean basins have provided a new approach to the tracing of water-mass and sediment movements. A good example is the monitoring of the cooling waters from the Hanford reactors in Richland, Wash. Following ^{65}Zn and ^{51}Cr down the Columbia River, scientists are able to observe the dispersion of the river water and its sediment once it enters the Pacific Ocean.[8] It has been possible over the years to determine the distribution and movement of sediments off the Washington coast by measurement of the ^{65}Zn activities associated with these deposits.[9]

Studies of beach erosion and migration of coastal sands have benefited significantly by the use of radionuclides. Sand particles have been tagged with ^{133}Xe and ^{140}Ba–^{140}La, for example, and their movements traced by scintillation detectors used either directly in the field or on samples taken to the laboratory.[10] Although more caution is required in handling radioactive tags, they prove more effective than stains because lower concentrations can be monitored and buried grains can be detected. However, caution and public opinion have restricted the use of this technique in many areas.

Nuclear Instrumentation

A goal of scientists is to monitor or measure the parameters of interest under natural environmental conditions. For the oceanographer this has become a reality in a few areas, as some of his sampling techniques have advanced from those of rather simple, crude devices to the more sophisticated electronic in-place measuring packages. The adaptation of nuclear techniques to problems in the marine environment is a recent development, which is still in its early stages but appears promising.

Current Measurements

Instruments based on the detection of radiation emitted by a radionuclide and determination of the amount present have been developed using both sealed and unsealed (tracers) sources for the in-place measurement of various parameters in both the water column and the sea floor. One approach, the injection of a tracer amount of radioisotope and determination of the rate and direction of its movement, is the basis of an instrument that has been used to measure current flow rates in the range 0.17 to 1.67 ft/sec (0.1 to 1.0 knot), with a theoretical lower limit of 0.002 ft/sec. This instrument consists of a wagon-wheel configuration with a series of detectors mounted on the wheel rim and an isotopic source located at the hub (Fig. 1). The radioisotope (^{131}I) is injected into the water, and the rate and direction of flow are determined by the time of arrival of the radioactivity at a particular detector.[11] Three slightly different models have been built and taken through various phases of testing. The instrument is known as the Deep-Water Isotopic Current Analyzer (DWICA).

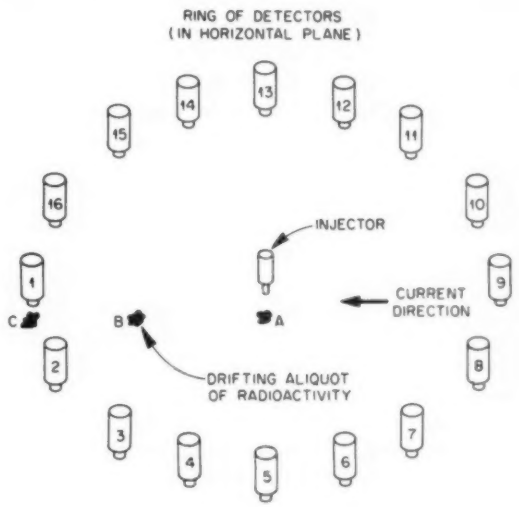

Fig. 1 Schematic diagram of DWICA operation.

Oxygen Determination

The oxygen content of seawater is of prime interest to the marine biologist. Its presence and amount noticeably control types and quantity of life sustained by the sea and thus are of major importance for assessing marine productivity. With a nuclear instrument the oxygen content in seawater can be measured in place. The instrument operates on a radioisotope-release principle[12] wherein the oxygen dissolved in the water reacts with radioactive thallium metal to release stoichiometric quantities of radioactive thallous ions. A Geiger tube capable of detecting ^{204}Tl beta rays serves as the brain center of the sensor. To ensure a uniform flow of water through the sensor, a pump is included in the instrument package.

Geological Measurements

The geological oceanographer has also been a beneficiary of recent advances in nuclear instrumenta-

tion, primarily in areas dealing with the mass physical and chemical characteristics of submarine sediments but also in investigations on suspended sediment in the water column.

Bottom-Sediment Density. Nuclear technology now makes it possible to conduct in-place measurements of sediment bulk density on the sea floor, with improvement in both the rate and accuracy of measurement. Since sediment cores do not have to be collected, many hours of laboratory testing are obviated.

The two types of instruments being used for these studies incorporate slightly different principles. In one,[13] a back-scatter system, a gamma-ray emitter (^{137}Cs) and a detector (G–M tubes) are housed in a single-barrel probe, which penetrates the sea floor in much the same way as a free-falling dart would enter the floor (Fig. 2). An internal driving mechanism moves the source–detector unit up and down inside the barrel, which is embedded in the sea floor. The density profile is obtained to a depth of 12 ft.

The other approach used to measure in-place density is based on attenuation of direct gamma-ray transmission.[14] Using a dual-barrel probe with a ^{137}Cs source in one barrel and a scintillation counter in the other, the density of the sediment between the barrels is readily determined by recording the gamma-ray attenuation. This particular probe is mounted on a tower, which is lowered slowly to the sea floor (Fig. 3). Once the tower is on the bottom, the probe is jacked into the sediment and the sensor output transmitted through a cable to the ship on the surface. This instrument is capable of providing a much more detailed density profile than the back-scatter device since measurements can be made in 0.5-in. increments to a depth of 10 ft. The back-scatter probe averages density over a 12-in. interval.

Using the same basic principle of measuring the attenuation of transmitted gamma rays as a measure of density, geological oceanographers can now measure sediment-density variation in cored samples that are still in the core barrel.[15] A ^{137}Cs source and a scintillation detector are mounted on a small cart in such a way that, as the cart is drawn along the length of the core barrel, the barrel with its sediment passes between the source and the detector. This instrument is capable of operating aboard ship as well as in the laboratory.

Suspended-Sediment Concentration. The sediment load carried by rivers and near-shore waters is of major importance to both marine geologists and coastal engineers, particularly in light of the cutting and filling that take place in such environments. The measurement of this load is difficult because instruments placed in the water interfere with the natural flow and thus distort the significance of the sediment-load measurement. A nuclear suspended-sediment concentration gage has now been developed which can detect

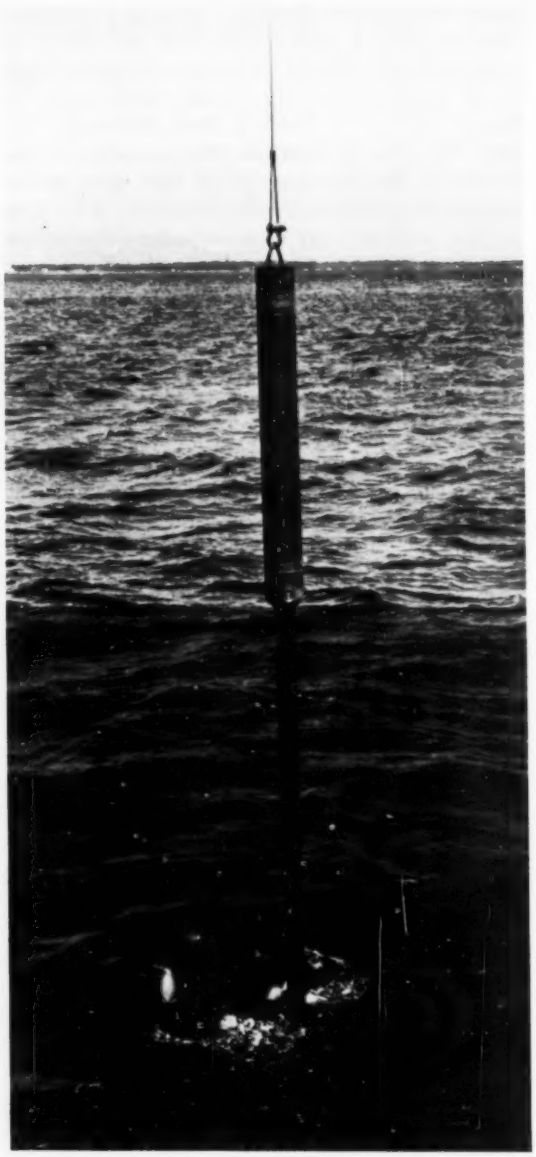

Fig. 2 Bottom-sediment density single-barrel probe.

Fig. 3 Bottom-sediment density dual-barrel probe.

concentrations as low as 500 ppm. The instrument consists of a ^{241}Am source and detector arranged so that the water passes between them, utilizing the attenuation of gamma rays as a measure of sediment concentration.[16] With slight modification it is expected that this instrument can be set in place and left unattended for several days at a time.

Sediment Analysis. With the increasing interest in sea-floor deposits, primarily for their economic values, the analyst requires a rapid technique for rough determination of the elemental compositions of these deposits. For the most part, the scientist is limited to collecting samples by remote techniques from a surface or submersible vessel and returning the samples to the laboratory for analysis. Efforts by the U. S. Atomic Energy Commission have shown that it may be feasible to adapt existing neutron activation systems to make in-place quantitative analyses on the sea floor.[17] Although several problems have yet to be solved, this approach holds much hope for a rapid assay technique in marine mining.

Nuclear Power Systems

Such unique characteristics of nuclear power systems as long life without refueling, no moving parts, and easy packaging for use in the oceans make them a very desirable power supply for certain oceanographic instruments. The oceanographer is tending more and more toward long-term observations, primarily by using large buoys, but a drawback to this arrangement is the power supply. The relatively short-lived batteries that are used today require either short observation periods or frequent battery replacement.

A few isotopic power systems have been put into operation, mainly to power remote weather stations or acoustic beacons on the sea floor.[18,19] There are, however, several isotopic power supplies under development for use with such instrument packages as navigational buoys, floating weather stations, and acoustic bench marks to be placed on the sea floor. The heat-producing characteristics of nuclear decay are also finding uses. Recently a miniature radioisotope-powered heat exchanger was built to heat and circulate warm water through a new type of suit used by scuba divers.[20,21]

Future Outlook and Uses

Undoubtedly, numerous applications of nuclear technology are yet to be conceived which could benefit the scientist in his studies of the sea. The problem to date has been primarily one of getting the nuclear scientist or engineer together with the oceanographer so that an exchange of ideas can take place. The instruments and techniques discussed above are examples of what can be done with proper communication between the concerned disciplines. With regard to

future developments in nuclear technology as related to oceanography, there appears to be a high probability for significant progress in several areas.

Recent studies indicate the feasibility of designing a probe that would utilize a fast-neutron source and suitable detector and be capable of penetrating the sea floor to measure the water content and porosity of submarine deposits.[22] Water content and porosity along with density are key parameters when considering the engineering properties (load-bearing capacity, slope stability, settlement) as well as the acoustical characteristics of the sea floor. Such a probe used in conjunction with the existing instrumentation would be of great importance as more structures are placed on the sea floor and as the capabilities for mining the sea bottom are more fully developed.

Another potential instrument is one that would be towed along the sea floor on a sledlike frame while measuring the bulk density of the underlying sediment. By using a large gamma-emitting source and the back-scatter technique already in use for density measurements, it may be possible to develop a technique for measuring variations in sediment density over large areas in a relatively short time.

In order to make sea-floor mining profitable, the exploration and exploitation costs must be decreased considerably, and one way to do this is to obtain rapid analysis and assay of bottom deposits. Activation analysis may provide the means of achieving this. It may become feasible to include a neutron activation-analysis system as part of the sledlike frame mentioned.

Another possible use for radioisotopes would be the tagging of the sludge solids that are being dumped into the ocean off most major coastal cities. Such tagging would provide a means of determining whether or not some of this material is returned to the local beaches and harbors.

As a by-product of nuclear technology, it may become feasible in some areas to use the warm water leaving a nuclear power plant to aid the fishing industry. If the plant should be sufficiently close to deep water, the warm water could possibly be piped out along the sea floor, debouching some distance offshore. The rising warm water would then lift the nutrient-rich bottom water to the surface. This water would provide the food supply needed to support a greater number of fish.

To promote and increase the number of users of nuclear techniques in oceanography, oceanographers and nuclear scientists and engineers must develop a greater understanding of each other's capabilities. From such efforts, radioisotopes and associated techniques undoubtedly will make significant contributions to the future of oceanography. (MG)

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A Review of Instrumentation and Procedures for ^{14}C and ^{3}H Radioassay by Thin-Layer and Gas–Liquid Chromatography

By Fred L. Snyder*

Abstract: *This review of instrumentation and procedures for radioassay by thin-layer and gas–liquid chromatography deals with basic techniques, equipment, typical results, and the advantages or disadvantages of each procedure. The thin-layer chromatographic techniques discussed are elution analysis, strip scanning, autoradiography, zone analysis, beta-camera detection, and combustion analysis. Radiometric procedures for gas–liquid chromatography include those using continuous-flow systems and those using collection systems that involve combustion and noncombustion techniques.*

This article reviews current radioassay instrumentation and radiometric procedures used with thin-layer chromatography (TLC) and gas–liquid chromatography (GLC). The theoretical and practical aspects of TLC and GLC, topics that are beyond the scope of this paper, are covered in Refs. 1 to 7 and 7 to 11, respectively. Chromatographic reviews are recommended for keeping abreast of these rapidly developing fields of analysis and their applications.[12-14]

The outline form used in this review permits quick retrieval of additional information from the scientific literature and from the commercial companies who sell the instruments described. The basic technique involved, examples of representative instruments or devices available, typical results, advantages or disadvantages of each technique, and literature references that provide details are described for each method. Specific applications of the various radiometric procedures are not discussed here, but can be found elsewhere.[12]

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Thin-Layer Chromatography

Thin-layer chromatography permits the chemist and biochemist to rapidly resolve organic and inorganic compounds by adsorption, partition, molecular filtration, and ion-exchange processes. TLC has found its greatest use in separations based primarily on adsorption, but its resolving power is increased by the fact that chemical reactions can be completed after chromatography in one direction and the derivatives formed resolved by chromatography in a second direction. Procedures of this sort are referred to as separation–reaction–separation TLC.

A brief outline of the steps involved in preparation of a chromatoplate, application of the sample, solvent development, and analysis in a thin-layer chroma-

tography system is given in Fig. 1. A suitable slurry of the adsorbent in water is prepared. Special applicators are commercially available for spreading the adsorbent slurry as a thin, uniform film (200 to 1000 μ) on glass, plastic, or aluminum surfaces. The layers are permitted

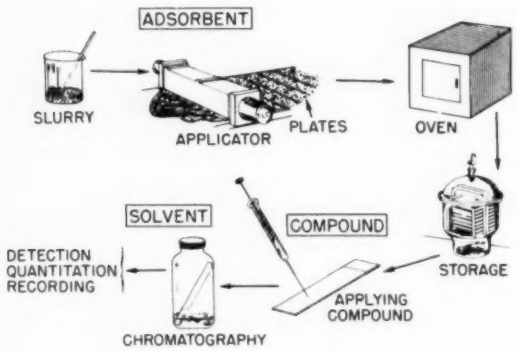

Fig. 1 Essential components of thin-layer chromatography systems.

to "set" for 5 to 10 min before they are activated in an oven; the degree of activation (removal of adsorbed water at the active sites) is controlled by the length of time of heating and the storage conditions after removal from the oven. Aliquots of samples (1 to 20 μl) are applied to one edge of the layer with micropipets or syringes. Larger volumes used with preparative TLC are generally applied to the adsorbent layer with automatic streaking devices. After the sample is dry, the chromatoplate is placed in a solvent chamber for development. The solvent chamber can be equilibrated (lined with filter paper saturated with the solvent mixture used for development) or nonequilibrated. Chromatograms develop faster, and the resolution of components is generally better in the equilibrated chambers; however, the rates of flow (R_f) are lower than in the nonequilibrated units. Development of the chromatogram is complete when the solvent front reaches a predetermined position, generally between 10 and 18 cm. The chromatoplate is then removed from the chamber, and the solvent is evaporated from the layer before visualization of the resolved components. There are three main methods for detecting the distribution of organic mass along the chromatographic lane: (1) spraying the layer with concentrated H_2SO_4 or dichromate–H_2SO_4 and then heating, (2) exposing the layer to iodine vapor, or (3) spraying with fluorescent dyes and viewing under an ultraviolet light. The principles and empirical guides for the selection of appropriate adsorbents and solvents to resolve specific chemical types can be found in the many books and reviews[1-7,12-14] available for TLC.

Modifications such as the addition of silver, arsenite, or borate ions to the adsorbent layers enhance the versatility of TLC, since these ions can participate in reversible reactions with organic compounds directly on the thin layers during chromatography. For example, silver ions can form π bonds with unsaturated aliphatic chains so that monoenes, dienes, trienes, etc., can be resolved in a stepwise manner. Arsenite and borate ions can form complexes with compounds having adjacent hydroxyl groups, and the resulting complexes can be resolved from isomeric forms that differ in the relative location of hydroxyl groups. Useful as adsorption TLC is, it generally requires other chromatographic procedures to resolve organic compounds belonging to a homologous series. One of the most successful procedures for this purpose is gas–liquid chromatography, which can subfractionate a homologous series according to molecular weight (carbon number), functional group, and degree of unsaturation.

Radiometric procedures for thin-layer chromatography have been reviewed[15-20] in considerable depth since the first published reports in the early 1960's. The methods are: (1) elution analysis; (2) strip scanning (G–M and scintillation detection); (3) autoradiography (direct, sublimation–distillation, and scintillation); (4) zone analysis (area scraping and zonal-profile scans); (5) beta-camera detection; and (6) combustion analysis.

Elution Analysis[21]

Technique. An area of adsorbent is loosened by scraping with a razor blade or spatula so that it falls on a filter disk in a tube or in a beaker. Extracting solvents are added to the adsorbent, and the mixture is passed through a filter (e.g., Millipore) having a pore size that is smaller than the adsorbent particles. Elutions are repeated until the sample is quantitatively recovered. Collections are also made with a glass tube, containing a fritted disk, that is connected to a water aspirator. The tube is inverted, and the adsorbent on the fritted disk is washed with appropriate solvents.

Equipment. Numerous devices for elution of samples from TLC adsorbents have been described, and many are commercially available. A tube containing a fritted disk (Fig. 2) and attached to a water aspirator is extremely useful in quantitative recoveries of the

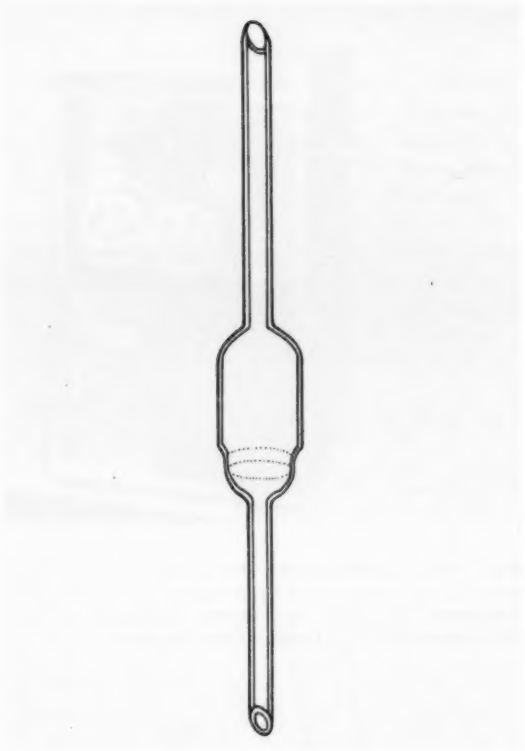

Fig. 2 Aspirator tube for collection of adsorbent and subsequent elution of labeled component from adsorbent. The disk is fritted glass.

adsorbent from the plate. However, the simplest procedure is merely to scrape with a razor blade.

Results. Knowledgeable choice of the eluting solvent is critical for quantitative recoveries. For polar compounds, the solvent polarity must be greater than that of the sample being eluted. Suitable solvents can be determined empirically by selecting a solvent or solvent mixture that causes the sample to migrate on the same adsorbent layer at an $R_f > 0.8$.

Advantages. (1) The compound is not destroyed* during radioassay and can be used for additional chemical analysis; (2) elution analysis is useful for isolation of large quantities of a compound; and (3) the apparatus required for this procedure is simple and inexpensive.

Disadvantages. (1) Selection of solvent(s) for quantitative elution is sometimes difficult or impossible; (2) adsorbents are sometimes difficult to remove from the eluting solvents; and (3) elution analysis is tedious if the entire chromatographic lane is to be quantitated for distribution of radioactivity.

Strip Scanning[22-47]

Technique. *Strip scanning* denotes a procedure in which a developed thin-layer chromatogram traverses a path under a radiation detector or between detectors. Although the detectors are generally fixed, occasionally the chromatogram is held stationary, and the detector moved. The latter arrangement is especially useful when radioactivity has a two-dimensional distribution on chromatograms. Detectors are thin-window G–M tubes, gas-flow G–M tubes, or phototubes. The phototube detector can be used only for radioassay of chromatograms that have been impregnated with scintillator gels or solutions after chromatographic development.

Equipment. The photoscanner (Fig. 3) is commercially available only in France. The G–M tube strip scanners (Figs. 4 to 6) are available from a number of

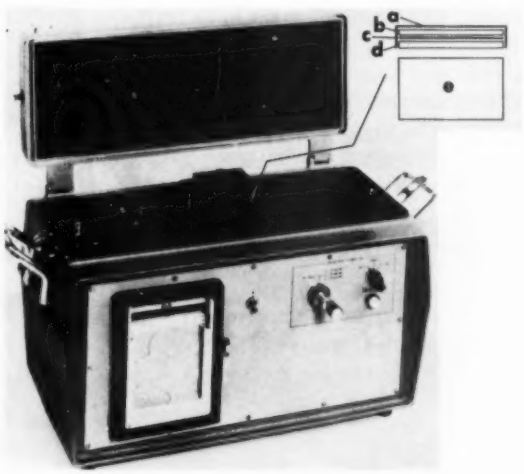

Fig. 3 A scintillation strip scanner for thin-layer radiochromatograms impregnated with organic scintillator: a, aluminum foil; b, scintillator gel; c, adsorbent; d, glass chromatoplate; e, photomultiplier. (Reproduced by permission of Société d'Applications Industrielles de la Physique, Paris, France.)

*i.e., the radioassay procedure per se is nondestructive; however, the compound is always subject to decomposition related to radiolysis (with the damage being insignificant at low specific activities) or to degradative changes occurring during chromatographic separation and processing.

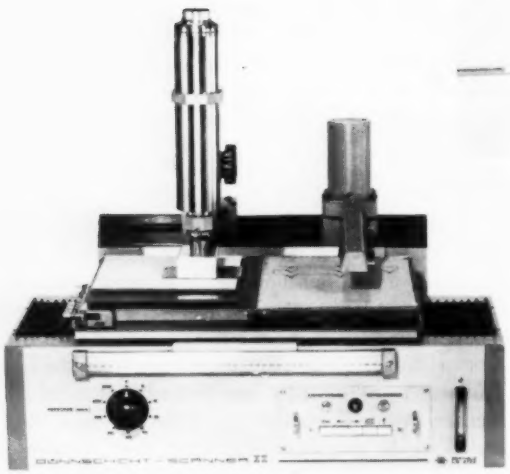

Fig. 4 Thin-layer chromatography strip scanner available from Laboratorium Prof. Berthold, 7547 Wildbad, Schwarzwald, Federal Republic of Germany.

Fig. 5 Paper chromatography strip scanner with a modified assembly for scanning 5 × 20-cm thin-layer chromatoplates. Instrument is available from Packard Instrument Co., Inc., 2200 Warrenville Road, Downers Grove, Ill. 60515.

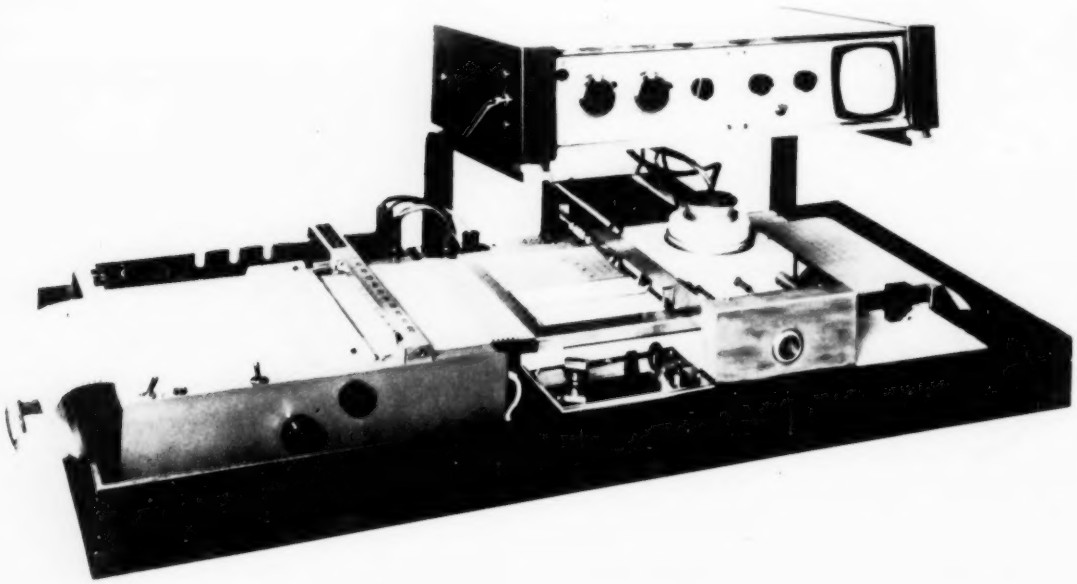

Fig. 6 A thin-layer radiochromatogram scanner that provides versatile presentation of data: tracings, integrated-count printout, or interval-count printout. Instrument is available from Panax Equipment Ltd., Redhill, Surrey, England.

commercial companies in the United States and Europe.

Results. The radioactivity along a thin-layer chromatographic lane can be shown as a linear display of the disintegrations per minute (dpm) or counts per minute (cpm) on chart paper when the radiation detector is connected to an appropriate recorder. In general, the recorder speed is adjusted to the same speed as that at which the TLC plateholder passes under the radiation detector. Such an arrangement permits easy location of the radioactive areas when the chromatogram is superimposed on the chart paper. Slower speeds provide adequate counting rates for good statistics at low levels of radioactivity on the chromatogram. A typical strip scan is shown in Fig. 7.

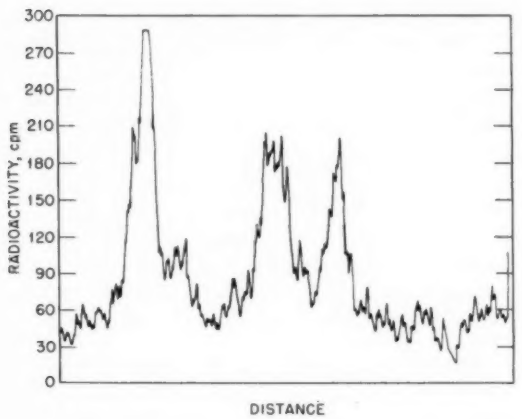

Fig. 7 A strip scan of ^{14}C-labeled compounds resolved on a thin-layer chromatogram.

Advantages. (1) Strip scanning gives a prompt record of the distribution of radioactivity on a chromatoplate; (2) the compounds are not destroyed during radioassay and can be used for subsequent chemical analysis; and (3) the technique is useful for measuring two-dimensional distribution of radioactivity on chromatoplates.

Disadvantages. (1) Strip scanning is not very sensitive for detecting low absolute quantities of low-energy beta isotopes, because there is self-absorption of beta energies in the adsorbent layer and because 4π detection is not possible on chromatoplates; and (2) the instrumentation is relatively costly.

Autoradiography[48-61]

Technique. Autoradiograms are prepared by placing the developed thin-layer chromatogram in direct contact with a photographic emulsion. X-ray films are generally used; however, in certain instances more sensitive emulsions, e.g., Kodak nuclear track emulsion type NTD or films having high ASA ratings, are best. The sensitivity of autoradiography can be even further increased by the impregnation of the adsorbent layers with nuclear emulsions or by fluorography.

Fluorography of chromatograms is accomplished by impregnating the TLC adsorbent with an organic scintillator such as anthracene; the light produced by the interaction of beta particles with the scintillator produces an image on the photographic emulsion that is in contact with the chromatogram. Fluorography has been shown to be only one-tenth as sensitive as impregnation with nuclear emulsions on paper chromatograms; no comparison with thin-layer chromatograms has been published. The fluorescence intensity of anthracene has been reported[53] to be enhanced by lowering the temperature, but this temperature effect is not appreciable for other scintillators.

Care must be taken to avoid chemical interaction between the adsorbent, solvent, etc. (nonradiation effects) in the chromatogram and the photographic emulsion. Sublimation and distillation of components from the adsorbent layer can also occur; some workers have taken advantage of these phenomena for increasing the sensitivity of detection of photographic emulsion procedures. Chemical interactions or distillation and sublimation effects can be circumvented by covering the adsorbent layer with Mylar or other thin plastic sheeting or preservative coatings (artist's fixative sprays); however, even the thinnest coverings or sprays decrease the sensitivity of detection and, in general, are unsuitable when, for example, tritium is assayed.

Equipment. The preparation of good autoradiograms requires a device that excludes light and provides maximum pressure contact between the adsorbent layer and the photographic emulsion. A number of simple holders for the preparation of photographic records of radioactivity distributed on thin-layer chromatograms have been described. A typical arrangement is illustrated in Fig. 8.

Results. An autoradiogram of a thin-layer chromatogram makes an excellent permanent record of the radioactive areas present. The relative sensitivity of the

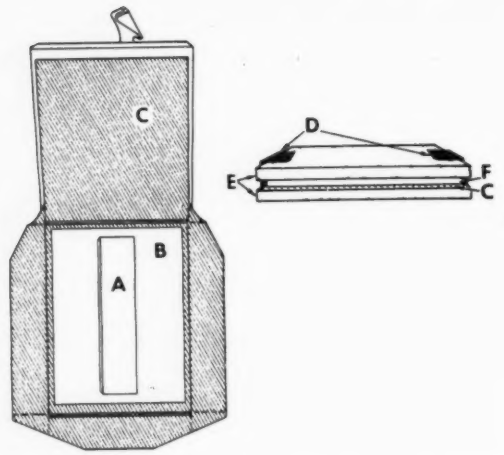

Fig. 8 A cassette used in the preparation of autoradiograms from thin-layer chromatograms: A, chromatoplate; B, Kodak no-screen X-ray film; C, envelope for holding film and chromatoplate; D, spring clip; E, 3/4-in. plywood plates; and F, 3/4-in. sponge.

procedure is governed by many factors, the most important of which is time. With sufficient time, the sensitivity of photographic emulsions in detecting radioactivity on chromatograms can be very great. A typical autoradiogram and photodensitometric scan of the developed photographic film are shown in Fig. 9.

Advantages. (1) Autoradiography is an extremely sensitive procedure for detecting low-energy beta-emitting isotopes, and (2) the apparatus required is inexpensive and simple.

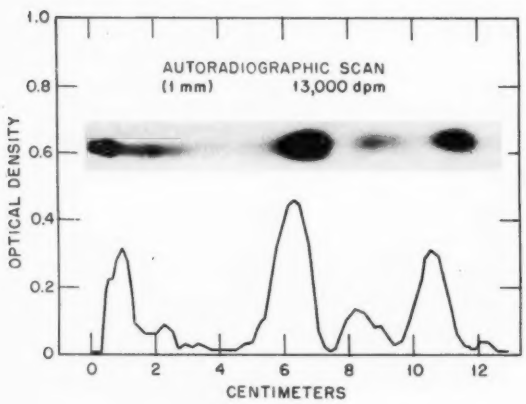

Fig. 9 A photodensitometric scan (1 mm) of an autoradiogram (developed film is shown above optical density curve) prepared from a chromatoplate used to resolve a mixture of ^{14}C-labeled lipids providing 13,000 dpm.

Disadvantages. (1) The procedure can require an extremely long time (months) for detecting low absolute quantities of low-energy beta-emitting isotopes; (2) certain steps of the procedure require a darkroom; (3) quantitative results are difficult to achieve; and (4) chemical interactions of compounds with the photographic films can cause false images.

Zone Analysis: Area Scraping[62-68] and Zonal Profile Scans[45,60,69-75]

Technique. The most sensitive quantitative procedure for detection and resolution of radioactivity on thin-layer chromatograms requires the scraping of zones across the chromatographic lanes for liquid scintillation radioassay. Entire spots or minute zones (1- and 2-mm width) are assayed by this technique. Care must be taken with polar compounds that are adsorbed on adsorbent particles to avoid absorption of beta energies, since the net effect is quenching. However, quenching effects can generally be avoided by using special scintillation solutions designed for assay of TLC adsorbents. Reduction of the particle size of the adsorbent to a dimension less than the path traveled by the beta particle or the use of quench correction factors based on internal or external standards can also be of help.

Equipment. Scraping of the TLC adsorbent into scintillation vials is readily accomplished by simply removing a spot area with a razor blade or spatula. However, when small zones (1- and 2-mm width) are collected to precisely determine quantitative distribution of radioactivity in complex mixtures, special instruments must be used. Precision instruments for scraping and collecting TLC adsorbents either manually or automatically have been developed by workers at Oak Ridge Associated Universities. The entire system of sample preparation and analysis has been completely automated, permitting a computer calculation and graphic printout of data derived from thin-layer radiochromatography. The device for automated sample preparation (Fig. 10) and the computer-analyzer system (Fig. 11) are shown. The automatic zonal scraper and collector is now commercially available (Analabs, Inc., 80 Republic Drive, North Haven, Conn. 06473).

Results. Radioanalysis of thin-layer chromatograms by zonal profile analysis is quantitative. A typical data sheet (Fig. 12) and a zonal profile scan

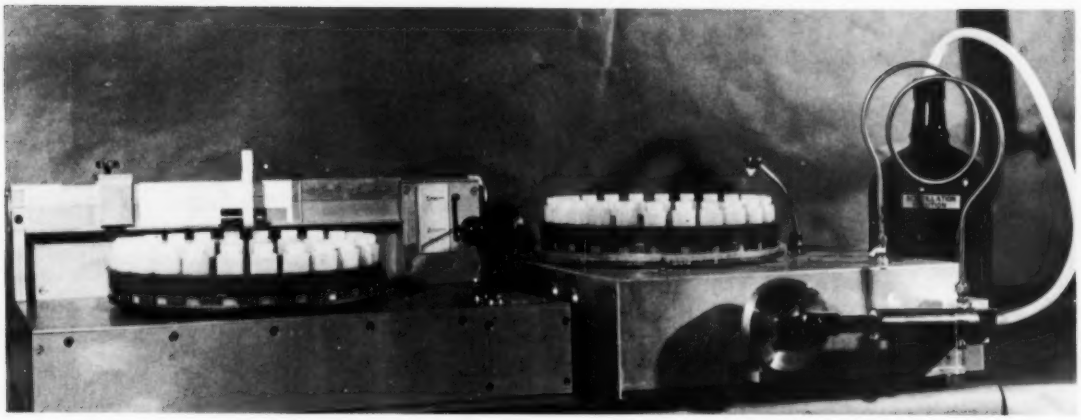

Fig. 10 An automatic zonal scraper and collector (left) and a pipetting device (right) used to prepare ^{14}C and ^{3}H zonal profile scans of thin-layer chromatograms. The automatic zonal scraper and collector is commercially available from Analabs, Inc., 80 Republic Dr., North Haven, Conn. 06473.

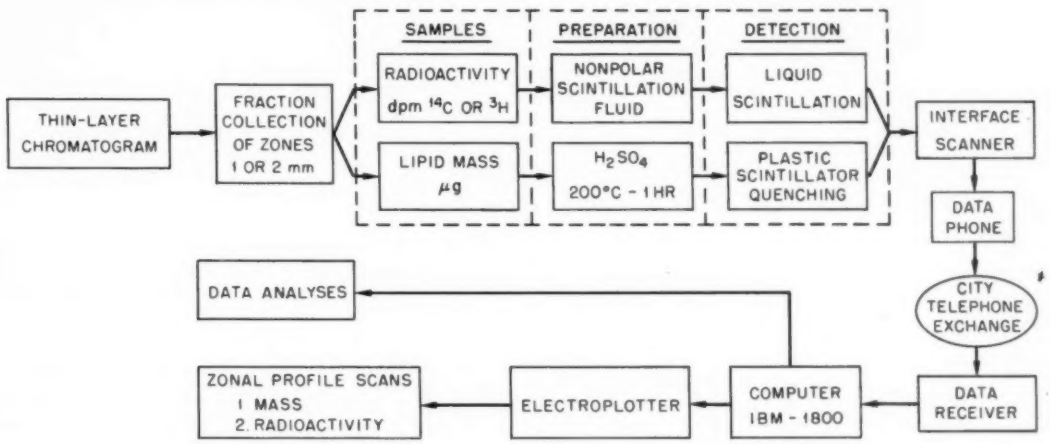

Fig. 11 A system designed for semiautomated and automated measurements of radioactivity and mass resolved on thin-layer chromatograms.

(Fig. 13) obtained from the computerized system are shown.

Advantages. (1) Of the available methods, zonal profile scanning provides the most sensitivity, best resolution, and most precise quantitation available for radioassay of thin-layer chromatograms; (2) the system is flexible—it can be manual or completely automated.

Disadvantages. (1) Samples cannot be recovered easily for further chemical analysis; (2) the large number of samples derived from zonal profile analysis can make the procedure time-consuming when the samples contain low absolute quantities of radioactivity; and (3) automated systems are relatively expensive.

Beta Camera

Technique. The newest instrument in radioassay of thin-layer chromatograms is the beta camera. The detector in this device consists of 1,622 picture elements equivalent to an equal number of individual

STEARYL-14C AL
EC-26-66

14C

15738.AVERAGE DIRECT ISOTOPE I

198.MEAN ISOTOPE I

15668	# TOTAL AREA UNDER CURVE									
8223	# AREA UNDER PEAK 1 FROM CENTIMETERS #	0.20	, DPM #	0.	TO CENTIMETERS #	1.40	, DPM #	73.CC
52.48	# PERCENT OF TOTAL AREA UNDER PEAK 1							
1089	# AREA UNDER PEAK 2 FROM CENTIMETERS #	1.60	, DPM #	108.CC	TO CENTIMETERS #	3.40	, DPM #	25.CC
6.95	# PERCENT OF TOTAL AREA UNDER PEAK 2							
549	# AREA UNDER PEAK 3 FROM CENTIMETERS #	3.60	, DPM #	30.CC	TO CENTIMETERS #	6.00	, DPM #	8 JC
3.50	# PERCENT OF TOTAL AREA UNDER PEAK 3							
3461	# AREA UNDER PEAK 4 FROM CENTIMETERS #	6.20	, DPM #	18.CC	TO CENTIMETERS #	8.80	, DPM #	74.CC
22.09	# PERCENT OF TOTAL AREA UNDER PEAK 4							
788	# AREA UNDER PEAK 5 FROM CENTIMETERS #	9.00	, DPM #	163.CC	TO CENTIMETERS #	10.00	, DPM #	26.CC
5.03	# PERCENT OF TOTAL AREA UNDER PEAK 5							
1277	# AREA UNDER PEAK 6 FROM CENTIMETERS #	10.20	, DPM #	30.CC	TO CENTIMETERS #	12.00	, DPM #	59 JC
8.15	# PERCENT OF TOTAL AREA UNDER PEAK 6							
272	# AREA UNDER PEAK 7 FROM CENTIMETERS #	12.20	, DPM #	76.CC	TO CENTIMETERS #	13.00	, DPM #	5.CC
1.74	# PERCENT OF TOTAL AREA UNDER PEAK 7							
99.56	# PERCENT RECOVERY							
8.94	# STANDARD DEVIATION							

14C

CPM	DPM
97	0.
92	0.
2560	903.
7848	2846.
7452	2700.
4414	1584.
421	117.
299	73.
395	108.
330	84.
399	109.

Fig. 12 A typical computer printout obtained from automated system depicted in Fig. 11.

gas-flow G–M tubes; the detector can operate with or without a 1.0 mg/cm^2 window. The entire chromatogram is placed on a special holder so that all the radioactivity distribution on the plate can be viewed at once on a cathode-ray imaging tube. A photographic record is made with a camera that is an integral part of the instrument. The chromatogram to be analyzed may be on glass, film, paper, or gel (up to 20 x 20 cm and 0.5 cm thick). Quantitative resolution is claimed for areas ranging from 0.04 to 64 sq. in.

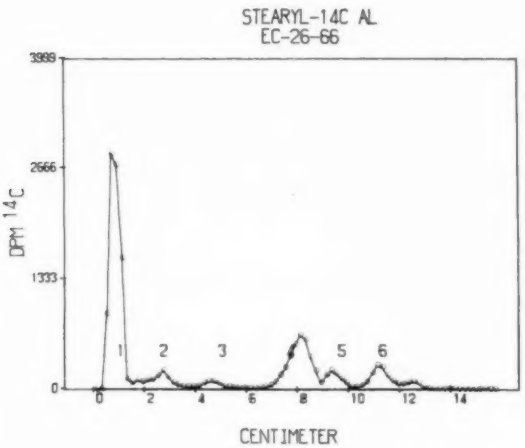

Fig. 13 A typical plot (zonal profile scan) of data processed from a liquid scintillation spectrometer, produced by a Benson-Lehner electroplotter.

Equipment. The beta camera is available only from Baird-Atomic (33 University Road, Cambridge, Mass. 02138). Model 6000 is pictured in Fig. 14; its approximate cost is $17,500.

Results. Data from the entire sample area are displayed on a cathode-ray tube. Figure 15 is the Polaroid photographic image of a typical "betagram." Precise readout counts are also provided for digital quantitation. The X–Y grid coordinates are used to select areas for quantitative preset-count or preset-time radioassay. The background is stated to be >0.5 count/min per detector in the beta camera.

Advantages. (1) The beta camera provides rapid analysis, including an instantaneous display of the radioactivity distribution on the entire chromatoplate; (2) compounds can be used for subsequent chemical analysis since they are not destroyed during radioassay; and (3) sensitivity for detecting low-energy betas is relatively good.

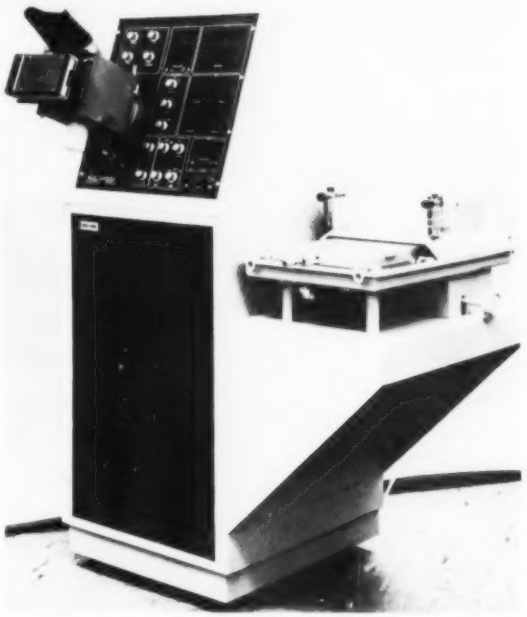

Fig. 14 The beta camera (Model 6000) available from Baird-Atomic, 33 University Rd., Cambridge, Mass. 02138.

Disadvantages. (1) The system uses extremely expensive instrumentation; and (2) the quantitation, resolution, and sensitivity of the beta camera are not as good as those attainable with liquid-scintillation–scraping techniques.

Combustion Analysis

Technique. This procedure is based on the quantitative conversion of organic matter to carbon dioxide and water for collection and subsequent radioassay. It has not yet been used for radioassay of thin-layer chromatograms although this has been suggested. A hydrogen-flame detector for mass detection on thin-layer chromatograms which has recently been described[76] could easily be adapted for radioassay. The CO_2 or H_2O liberated by the hydrogen-flame detector or by the combustion of TLC adsorbent zones could be collected for radiometric measurements in a liquid scintillation spectrometer.

Instrumentation. None available.

Results. None available

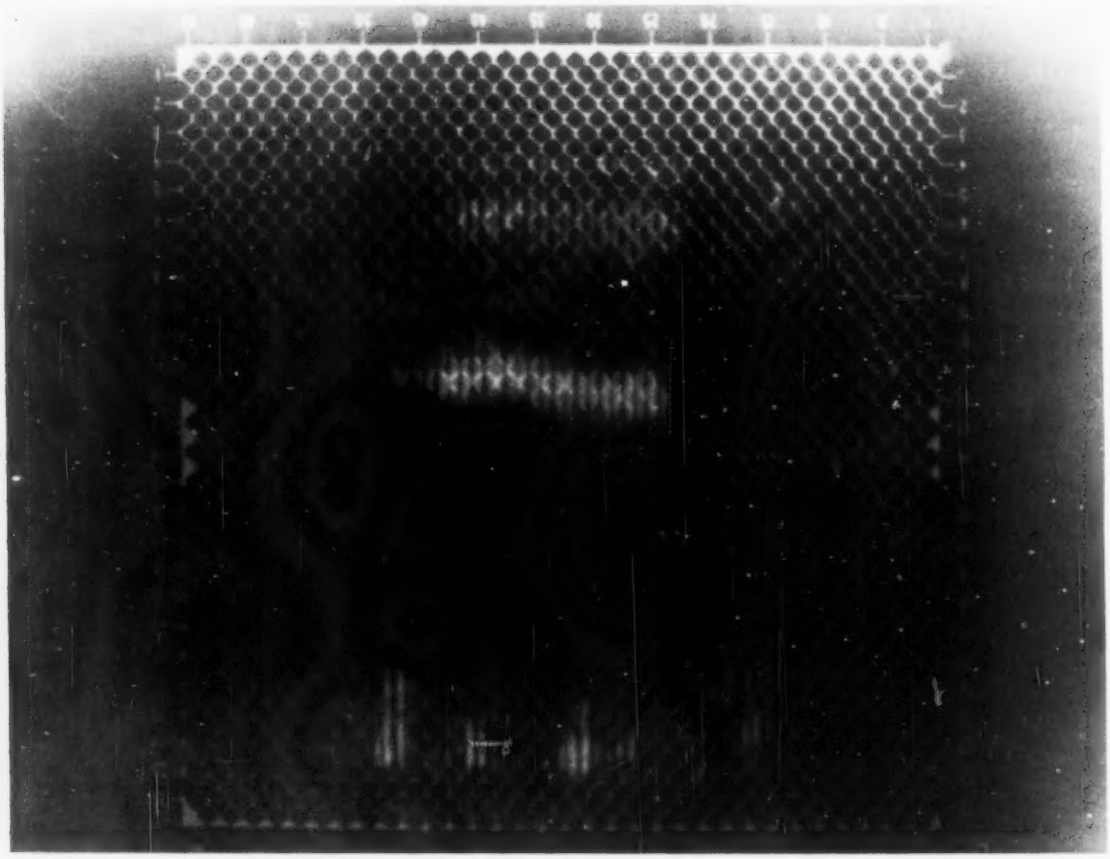

Fig. 15 A betagram prepared from a thin-layer chromatogram containing a standard mixture of ^{14}C-labeled compounds. It was obtained with the Model 6000 beta camera; light areas on the dark background designate the radioactive areas on the chromatoplate.

Advantages. (1) This system would circumvent quenching or self-absorption problems associated with other TLC radioassay procedures, and (2) high sensitivity is theoretically possible.

Disadvantages. (1) The technique would be extremely cumbersome unless automated; (2) destruction of the compound used for radioassay would prevent subsequent chemical analysis; and (3) the initial costs for development of instrumentation could be high.

Gas–Liquid Chromatography

Gas–liquid chromatography (GLC) separates volatile organic compounds of a homologous series according to functional groups, molecular weight, chain lengths, and degree of unsaturation. Separations are based on the partition (and interaction) of compounds between the gas phase and liquid coating on an adsorbent support. In general, most organic compounds are converted to derivatives of lower vapor pressure before GLC. However, excellent resolution and quantitation using temperature programming have been obtained for compounds of relatively high molecular weight (~1000) without preparing derivatives.

The basic components of a gas–liquid chromatograph designed for radioassay measurements are shown in Fig. 16. The sample is injected into a flash heater, at a temperature higher than that of the column, which vaporizes the components before passage into the column containing the packing mate-

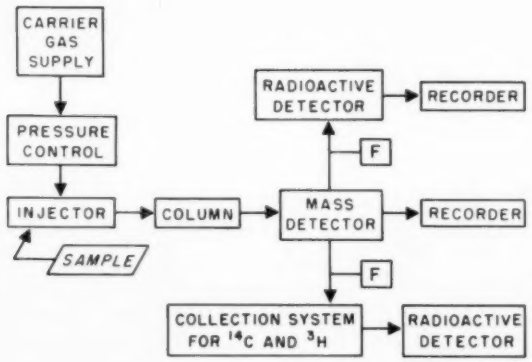

Fig. 16 Diagram of a gas–liquid radiochromatography system. The gas stream exiting from the mass detector can be directed to a continuous-flow system (arrow pointing up) or to a collection system (arrow pointing down). Both systems have the option of passing the gas stream through a furnace (F) for combustion of organic components with suitable catalysts.

rial. The packing consists of an inert support coated by a liquid phase; the liquid phase may be either polar or nonpolar. Nonpolar phases are used when separation of compounds of differing molecular weight is desired; the resolution of compounds on the basis of chain length, degree of unsaturation, and functional groups requires the use of polar phases. The mass of compounds leaving the column can be measured by hydrogen-flame ionization, argon ionization, thermal-conductivity electron capture, or density-balance detectors. Radiometric measurements require a specialized detection system on line with the gas flow leaving the column or collection devices. Some of the detection devices for measuring radioactivity require that the samples first be converted to $^{14}CO_2$ and $^{3}H_2O$ (or reduced to $^{3}H_2$) by appropriate procedures. For this reason, the instruments designed for continuous-flow systems and for collection systems in GLC radioassay are discussed under the subheadings of combustion and noncombustion techniques. The only earlier review of the analysis of radioactive compounds by gas–liquid chromatography was written by Karmen.[77]

Continuous-Flow Systems

Combustion Procedures

Technique.[78–88] The exit from the mass detector or column of a gas–liquid chromatograph is connected by a high-temperature line to a furnace at 750°C containing a tube filled with CuO, Co_3O_4, or other metal oxides and, generally, also a tube filled with iron filings. Organic components in the gas stream are quantitatively converted into CO_2 and H_2O as they are passed over the CuO; the water is reduced to tritium gas in the tube containing the iron. The $^{14}CO_2$ and $^{3}H_2$ gases can then be transported at room temperature to the radiation detector. Detectors used for radioassay of the gas stream containing $^{14}CO_2$ or $^{3}H_2$ (or both) are anthracene columns in liquid scintillation sample-counting chambers, ionization chambers, or proportional counting G–M tubes. The last procedure requires that the radioactive gas stream be mixed with methane. Long-lasting memory effects must be prevented in such systems, since the buildup of residual background decreases the sensitivity and accuracy of the radioassay measurement. Moreover, memory effects must be minimized if successful sequential analysis is to be achieved rapidly.

Equipment. A number of special furnaces for the combustion of samples to $^{14}CO_2$ and $^{3}H_2$ are commercially available. Examples of different radiation detectors that are available for continuously monitoring gas streams from a gas–liquid chromatograph are shown in Figs. 17 to 19.

Results. Data originating from continuous-flow systems that detect radioactive $^{14}CO_2$ or $^{3}H_2$ are generally displayed on strip-chart recorders attached to rate meters on line with the radiation detector. The strip-chart display is similar to that illustrated in Fig. 20. Digital-output devices to give the instantaneous integration of peak areas can also be included as a part of these systems.

Advantages. (1) Combustion technique permits transport of gases to radioactive detector at room temperature; (2) the radiation detector need not be heated; and (3) a wide variety of radiation detectors can be used in this system.

Disadvantages. (1) Combustion destroys the compounds radioassayed, preventing subsequent chemical analysis; (2) quantitative combustion can be a problem; and (3) combustion-flow cell detectors are relatively expensive compared with most collection devices.

Noncombustion Procedure[89–98]

Technique. This procedure consists merely of passing the hot gas stream from the mass detector directly into a radiometric detection system. It necessitates maintaining a temperature high enough to keep

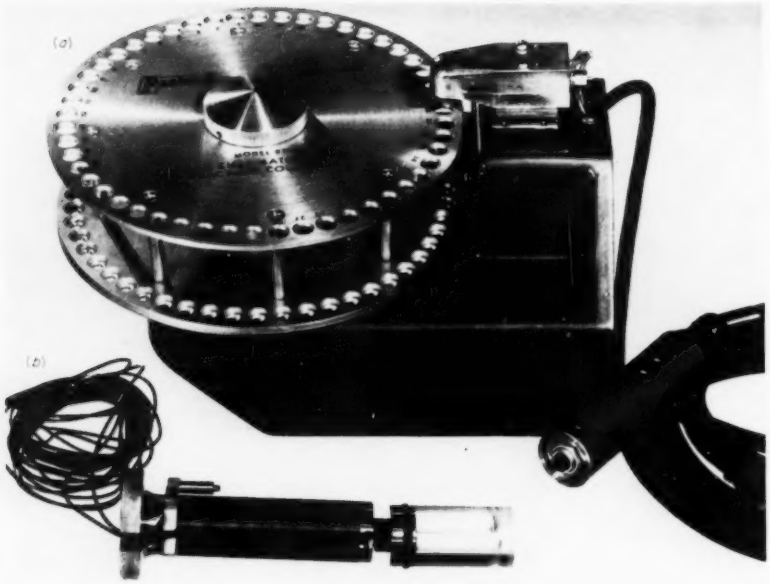

Fig. 17 Commercial instruments (a) for collection of labeled compounds by condensation on anthracene and (b) for measurement of $^{14}CO_2$ and $^{3}H_2$ passing over an anthracene column inserted into a liquid scintillation counter. Both devices are available from Packard Instrument Co., Inc., 3200 Warrenville Road, Downers Grove, Ill. 60515.

all compounds volatilized until the radioassay measurement has been completed. Continuous trapping of the components in the hot gas stream has been carried out directly in containers of liquid scintillation solutions located in the phototube chamber of liquid scintillation spectrometers. A flush-out system enables the operator to replace the scintillation fluid with a fresh supply when residual radioactivity builds up to undesirable levels.

Equipment. Continuous monitoring of the unprocessed gas stream in a collection device (scintillation fluids) or flow-through detectors (ionization chambers or G–M type) has not been as popular a technique as that involving combustion of compounds for flow-through cell monitoring. However, such instrumentation (Fig. 19) has been described in the literature and is marketed.

Results. Data originating from the continuous monitoring of a collection device are displayed as a stepwise curve on strip-chart recordings. Replacement of the scintillation fluid during the collection intervals returns the recording pen to the base line. Typical results obtained with a high-temperature flow-through device and an ionization detector are illustrated in Fig. 20.

Advantages. (1) The noncombustion system is generally simpler than combustion–flow cell detectors since combustion furnace and accessories are not required; and (2) in some systems, the compounds can be collected for subsequent chemical analysis.

Disadvantages. (1) Memory effects (buildup of background radioactivity) can occur; (2) compounds must be kept volatile until they leave the radiation detector; (3) the radiation detector must be heated to maintain volatility of most compounds; and (4) the procedure is relatively expensive compared with most radiometric collection techniques.

Collection Systems

Combustion Procedures[99]

Technique. This procedure has been used only for radioassay of $^{14}CO_2$. The basic combustion procedure is identical to that used in continuous monitoring systems; i.e., the gas stream from the GLC mass detector is passed over CuO at >700°C. However, the $^{14}CO_2$ released is then collected in scintillation vials, containing Hyamine or some other CO_2 adsorbent, at preselected times based on emergence of individual components from the mass detector. Appropriate volumes of liquid-scintillation solutions are added to the vials containing the collected $^{14}CO_2$ for subsequent measurement in a liquid-scintillation spectrometer.

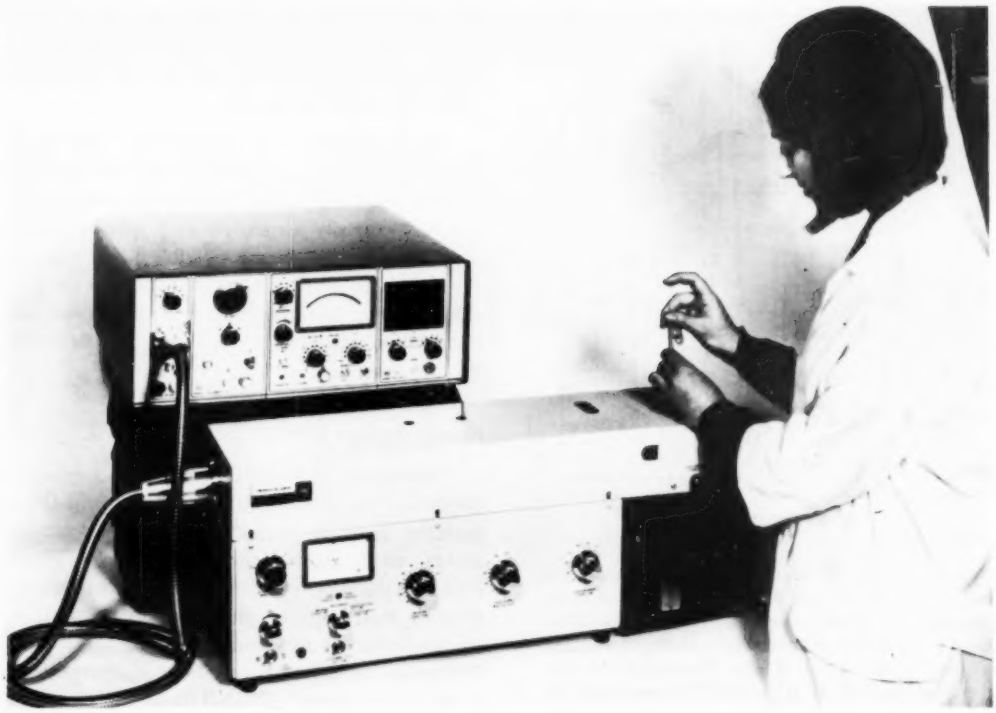

Fig. 18 Gas–liquid radiochromatography instrumentation containing a continuous-flow reaction tube with proportional counter tube (Model RGC 170) available from Laboratorium Prof. Berthold, 7547 Wildbad, Schwarzwald, Federal Republic of Germany, and Perkin-Elmer Instrument Division, Danbury Rd., Norwalk, Conn. 06852.

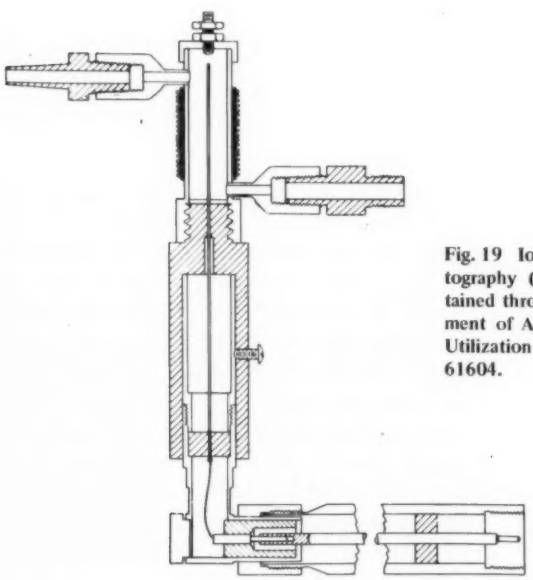

Fig. 19 Ionization chamber for high-temperature gas chromatography (see Refs. 89 and 91 for details). Photograph obtained through the courtesy of Dr. H. J. Dutton, U. S. Department of Agriculture, Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Ill. 61604.

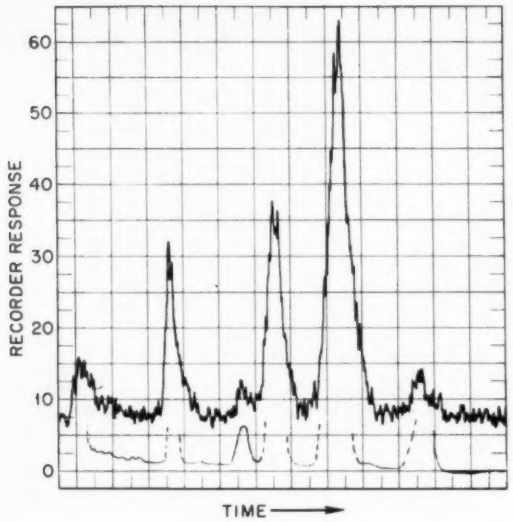

Fig. 20 Typical results obtained from the analysis of ^{14}C-labeled compounds resolved by a gas–liquid chromatograph utilizing an ionization chamber for radiation detection. The dark curve represents radioactivity, and the light curve represents mass (see Ref. 89 for details). Photograph obtained through the courtesy of Dr. H. J. Dutton, U. S. Department of Agriculture, Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Ill. 61604.

Equipment. The $^{14}CO_2$ gas stream from the combustion furnace is directed into the vial containing the CO_2 adsorbent by a piece of tubing attached to a hypodermic needle. A brief description[99] of this arrangement follows:

> The chromatographed sample passed through the effluent heater and over CuO in a stainless steel tube (¼ in. outer diameter) into a 735°[C] combustion furnace regulated with the controls and heating element of a Packard Tri-Carb Combustion Furnace, Model 325. This system combusted all organic material to water and CO_2. The $^{14}CO_2$ was carried through Tygon tubing (15 in. × ¼ in. inside diameter) to a No. 18-gauge hypodermic needle and bubbled through 4 ml hydroxide of Hyamine in a liquid scintillation-counting vial. A scintillation solution (15 ml) was added, and the amount of ^{14}C radioactivity determined.

Results. Recoveries of ^{14}C-labeled fatty acids by this procedure have been reported to be quantitative (to within 5%).

Advantages. (1) Combustion permits transport of gases to collecting device at room temperatures; (2) collection techniques provide greater sensitivity and higher precision than continuous-flow systems, because low-activity samples can be counted for extended periods; and (3) there are no problems associated with the formation of aerosols and the difficulty in quantitatively collecting aerosols.

Disadvantages. (1) Combustion–collection procedures are time consuming compared with systems with flow-through cells; (2) the radioactivity collected is not necessarily associated with specific GLC peaks since inherent errors are possible when relating continuous recordings of mass detection to radioactivity trapped at predetermined collection periods; and (3) combustion destroys compounds radioassayed, preventing subsequent chemical analysis.

Noncombustion Procedures[100–105]

Technique. Fractions containing organic components in the effluent gas stream from the GLC mass detector may be trapped in cartridges containing anthracene or cellulose, in scintillation vials containing liquid scintillation solutions, or in glass tubes with or without inert supports that increase the surface area for condensation and adsorption. The aerosols formed during the cooling and condensation of organic matter in the gas stream are difficult to collect quantitatively, but the devices used for this purpose have minimized the problem.

Equipment. Collection turntables for collection of GLC samples in individual anthracene cartridges (Fig. 17) or directly in counting vials containing liquid scintillation solvent (Fig. 21) have been described. A manual device for direct collection (in scintillation fluids) of radioactive samples that exit from the GLC mass detector is shown in Fig. 22. Only the turntable system using anthracene cartridges is commercially available.

Results. Data from the noncombustion collection systems are reported as radioactivity present in mass peaks (specific activity); a plot of data obtained in this system is illustrated in Fig. 23. Recoveries of radioactivity by noncombustion procedures are >90%.

Advantages. (1) Noncombustion procedures require relatively simple and inexpensive equipment; (2) noncombustion collection procedures have higher sensitivity and higher precision than continuous-flow systems, because low-activity samples can be counted for extended periods; (3) the technique lends itself to semiautomatic procedures; and (4) the labeled compounds collected can be recovered for subsequent chemical analysis.

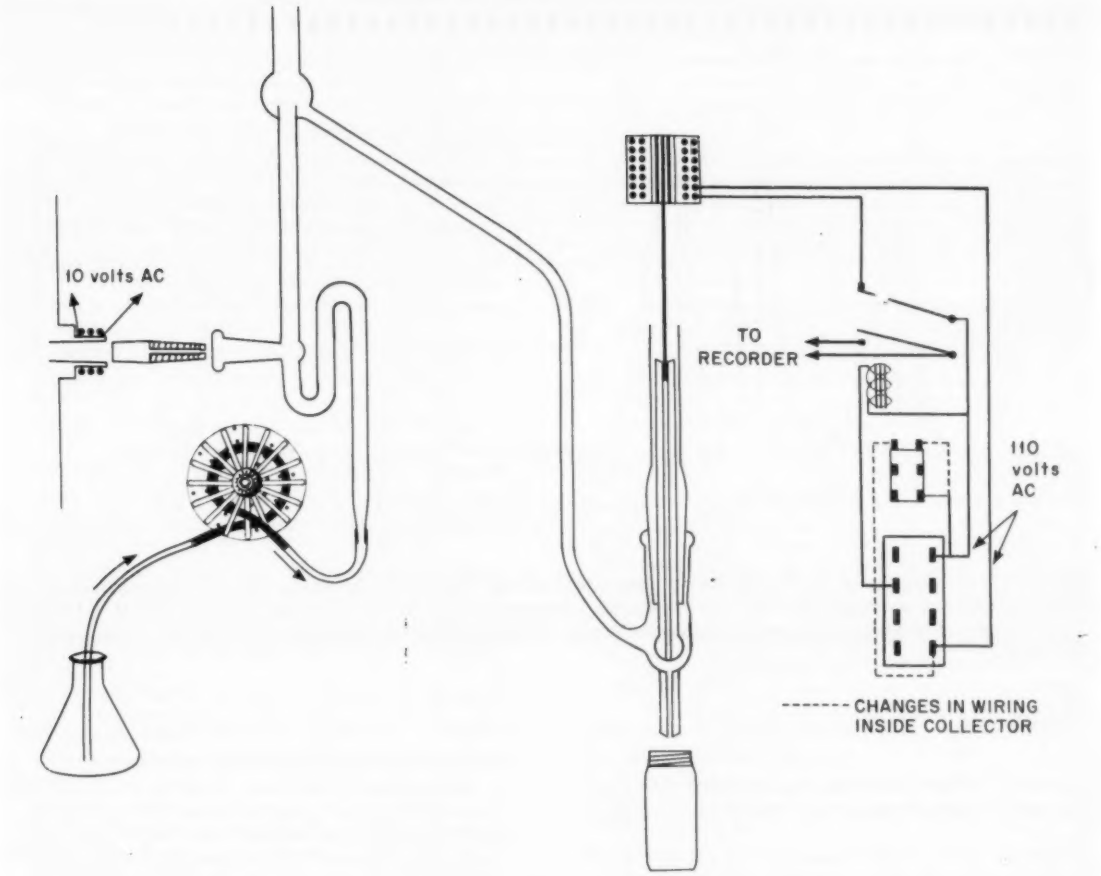

Fig. 21 An automated system for collection of radioactivity leaving the mass detector of a gas–liquid chromatograph. Collections are made directly in counting vials by condensation in the scintillation solvent (see Ref. 102 for details). Photograph was obtained through the courtesy of Dr. H. J. Dutton, U. S. Department of Agriculture, Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Ill. 61604.

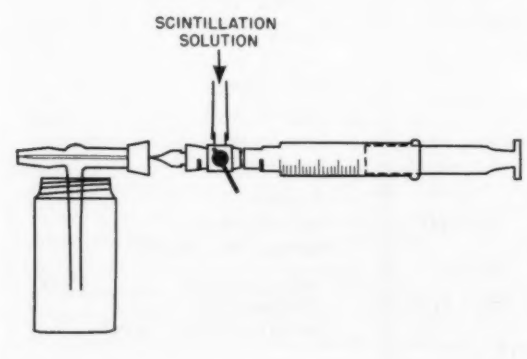

Fig. 22 A device for the manual collection of labeled components resolved by gas–liquid chromatography. Collections are made directly in counting vials by condensation in the scintillation solvent. Photograph obtained through the courtesy of Dr. H. J. Dutton, U. S. Department of Agriculture, Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Ill. 61604.

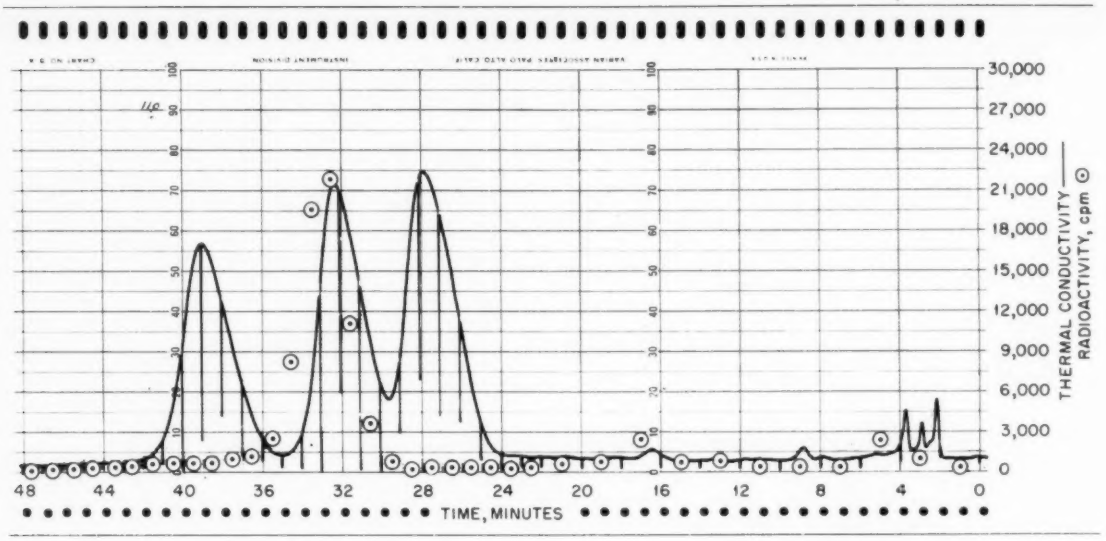

Fig. 23 A typical plot of mass and radioactivity data obtained by gas–liquid chromatography when the radiometric data are based on collection techniques (see Ref. 102 for details). Photograph was obtained through the courtesy of Dr. H. J. Dutton, U. S. Department of Agriculture, Agricultural Research Service, Northern Utilization Research and Development Division, Peoria, Ill. 61604.

Disadvantages. (1) Aerosols formed at high temperatures are difficult to trap quantitatively; and (2) the activity collected may not be associated with GLC peaks since inherent errors may occur when relating continuous recordings of mass detection to radioactivity trapped at predetermined collection periods.

(FEM)

Appendix

Some Companies Selling Radioassay Equipment for Thin-Layer and Gas–Liquid Chromatography

1. Analabs, Inc. TLC
   80 Republic Dr.
   North Haven, Conn. 06473
2. Baird-Atomic, Inc. TLC
   33 University Rd.
   Cambridge, Mass. 02138
3. Brinkmann Instruments TLC
   Cantiague Rd.
   Westbury, N. Y. 11590
4. Desaga TLC
   Postfach 407
   69 Heidelberg 1
   Federal Republic of Germany
5. Frieseke & Hoepfner GmbH TLC
   852 Erlangen-Bruck
   Federal Republic of Germany
6. Laboratorium Prof. Berthold TLC, GLC
   7547 Wildbad
   Schwarzwald
   Federal Republic of Germany
7. Perkin-Elmer Instrument Div. GLC
   Danbury Rd.
   Norwalk, Conn. 06852
8. Nuclear-Chicago Corporation TLC, GLC
   333 E. Howard Ave.
   Des Plaines, Ill. 60018
9. Nuclear Supplies TLC
   Box 312
   Encino, Calif. 91316
10. Packard Instrument Co., Inc. TLC, GLC
    2200 Warrenville Rd.
    Downers Grove, Ill. 60515
11. Panax Equipment Ltd. TLC, GLC
    Redhill, Surrey
    England
12. Philips TLC
    Eindhoven
    Netherlands
13. SAIP TLC
    38 Rue Gabriel-Crie Malakoff
    Paris, France
14. Tracerlab TLC
    1601 Trapelo Rd.
    Waltham, Mass. 02154
15. Varian Aerograph TLC
    2700 Mitchell Dr.
    Walnut Creek, Calif. 94598

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DART Radioisotope Thruster

A radioisotope thruster applicable for reaction-control systems on future military spacecraft has successfully passed its ground demonstration test. The test was a key milestone in the Decomposed Ammonia Radioisotope Thruster (DART) exploratory development program being conducted by the Systems Group of TRW Inc. for the Air Force Rocket Propulsion Laboratory at Edwards Air Force Base in California. TRW is to study potential unmanned missions for the low-thrust DART system; determine the performance characteristics of DART for those missions; and design, build, and demonstrate a flightweight thruster using radioisotope power. Mission and performance studies have shown that the DART system has weight and reliability advantages for spacecraft attitude control and station keeping. A year-long test at operational temperatures is now in progress at Mound Laboratory in Ohio.

The basic DART configuration (Fig. 1) includes an encapsulated radioisotope heat source ($^{238}PuO_2$), one to four nozzles with a separate flow tube for each nozzle, passive thermal control, and a reentry

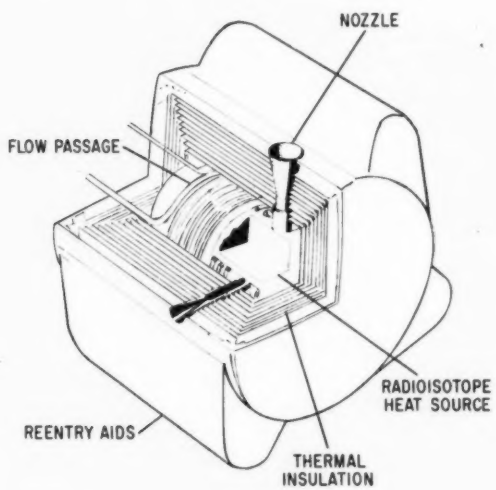


Fig. 1 DART configuration.

module. Energy from the decay of the radioisotope heats and completely decomposes the ammonia propellant before expansion through a nozzle. Ammonia has a theoretical optimum specific impulse of 305 sec at 2000°F. DART is designed to operate in either the pulsed or continuous mode and can produce more than 100 millipounds of thrust. The DART heat source is also attractive for high-temperature radioisotope space power systems.

Aerospace nuclear safety requirements are stringently adhered to. The system is designed to completely contain the isotope fuel under all credible accident possibilities, including reentry and earth impact, and for a reasonable time following impact, on land or in shallow water, to permit search and recovery. (MG)

^{90}Sr Beta Irradiator

Minnesota Mining and Manufacturing Company (3M) is offering a beta irradiator (Fig. 1) with a 100- to 500-curie ^{90}Sr source. The irradiator is provided in a nickel-plated stainless-steel shield with outer dimensions of approximately 12 in. dia. by 15 in. high; the shield thickness is 4 in. With its weight of about 500 lb, the irradiator is a convenient device for laboratory use. The price varies from $4000 with a 100-curie source to $7000 with a 500-curie source. Delivery is within 3 to 4 months.

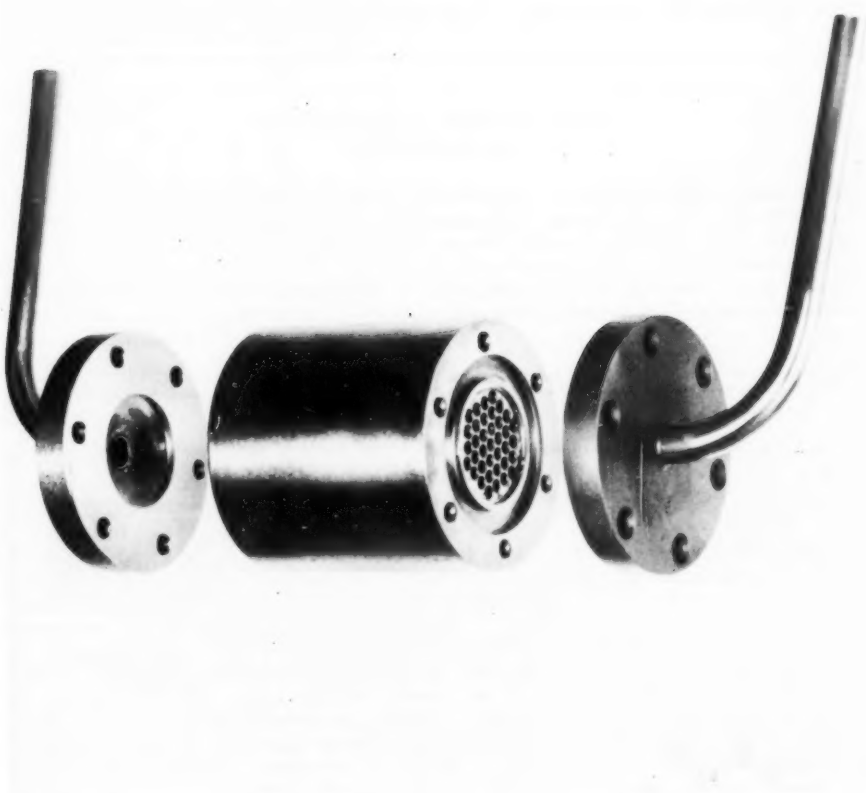


Fig. 1 The 3M ^{90}Sr beta irradiator.

One hundred curies of ^{90}Sr will deliver a dose in excess of 0.5 Mrad/hr to 50 g of unit-density material. Larger amounts of material may be circulated through the irradiator to receive the same dose over a longer period of time. Material may be added or samples taken from it at any time, and the material may be heated or cooled during a run. The unit may be used not only in developing a chemical process but also for obtaining data to determine if a process is economically feasible.

The ^{90}Sr is adsorbed on "microspheres"—extremely small ceramic beads. The microspheres are insoluble in all common reagents except hydrofluoric acid. The softening point is about 1500°C, and they are not damaged by high radiation doses. (MG)

Determination of Particle-Size Distribution by Beta Backscattering

An instrument is on the market* which determines particle-size distribution in a sediment by the beta-backscattering technique. The instrument contains a $^{90}Sr-^{90}Y$ source whose beta-radiation beam is directed onto the bottom of a chamber in which the sediment is suspended in a suitable liquid. The intensity of a backscattered radiation is proportional to the thickness of the layer of material from which the radiation is scattered, as well as to the atomic number of the material. Hence the sedimentation rate, which is a function of particle size, is indicated by the backscattered-radiation intensity, recorded by suitable ancillary instrumentation. (MG)

*Summation Electronics Ltd., handled by Greenray International, 840 West Church Rd., Mechanicsburg, Pa. 17055.

Isotope Technology on Postage Stamp

By David Wolf*

A recent Israeli airmail stamp (Fig. 1) recognizes the separation by fractional distillation and thermal diffusion of heavy oxygen, a significant Israeli export. The process is based on research and development carried out for many years at the Weizmann Institute. Enrichments of ^{18}O up to 99% and ^{17}O up to 88% were achieved. These enriched stable-isotope products are widely used as tracers, because radioisotopes of oxygen are too short lived for convenient application. The heavy oxygen is also used by Miles-Yeda Ltd. in Rehovoth, Israel, to produce chemical compounds labeled with heavy oxygen. (MG)

*Weizmann Institute of Science, Rehovoth, Israel.

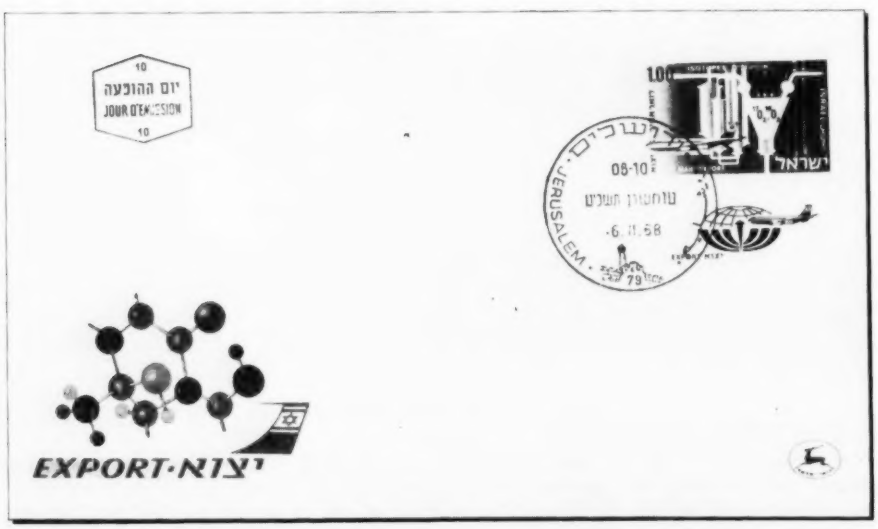


Fig. 1 First-day cover of letter with "isotope" stamp.

Radioisotope Ice-Warning Indicator for Aircraft

An ice-warning indicator that contains a beta-emitting radioisotope has been patented* by four Russians. Mounted on the aircraft wing, the instrument housing serves as an ice-formation surface. Inside the housing is a ^{90}Sr source. Its beta-radiation beam crosses the ice-formation surface obliquely to reach a Geiger–Mueller counter, which indicates the presence of ice by the change in radiation intensity detected. So that operation may be intermittent, a heater is interposed between the source and ice layer. The electronic arrangement is such that when the ice is 0.1 to 0.5 mm thick, the decreased radiation transmission results in current flow through the heater. The ice melts until the surface is clear; then the heater turns off and icing recommences. (MG)

*S. S. Emelyanov, K. E. Polischuk, M. V. Dmitriev, and V. I. Rogachev, Ice-Warning Indicator, British Patent No. 1,090,920, Nov. 15, 1967 (filed Nov. 3, 1965, No. 46505/65).

The Fission Products

By Françoise Laveissiere, Chap. 5, pp. 1024-1049 (in French), in *Nouveau Traité de Chemie Minérale,* Vol. 15, No. 4, P. Pascal (Ed.), Masson et Cie, Paris, 1967.

This review of 335 references discusses various processes for recovery of a number of the more important and useful fission products from nuclear fuel processing waste. Schematic flowsheets of the American, British, Japanese, and French recovery processes are presented, and actual and possible applications of recovered fission products are listed. (MG)

Radioisotopes in the Pulp and Paper Industry

Report of Panel, Helsinki, 1967
IAEA, Vienna (STI/PUB/202)

Fifty-five persons from 10 countries attended a panel discussion in Helsinki, Finland, on the use of radioisotopes in the pulp and paper industries. Papers were presented and discussions held on instruments that use radioisotopes, tracer applications, the use of radioisotopes to eliminate static electricity, and radioisotope sources of radiation for use in processing.

The panel concluded that, although radioisotope techniques are routinely used in the pulp and paper industries of some countries, there is still a gap in communicating information on these methods to potential users. They recommended that the International Atomic Energy Agency (IAEA) work toward publication in the pulp and paper industry journals of review papers covering these techniques. Some of the techniques could be beneficially applied in the developing countries where there are pulp and paper industries. The panel also recommended that the Agency work toward uniformity in health and safety regulations concerning radioisotope uses. Since new paper-making processes are being developed, gage requirements may become quite different and new measuring methods and narrower tolerances desirable. Therefore it was recommended that the Agency convene another meeting later to prepare both users and manufacturers for any necessary design changes. (MG)

Section III

Isotopes and Radiation Technology

Process Radiation Development

Textile Polymers: Effects and Application of Nuclear Radiation

By P. Rochast

Abstract: *The literature (43 references) is reviewed on the effects of nuclear radiation on natural and man-made fibers and the means by which this radiation may be used to impart new properties to such fibers by radiation grafting.*

Three different types of reaction may occur when a molecule AB is exposed to high-energy radiation:

$AB \rightarrow AB^+ + e^-$ (simple ionization)
$AB \rightarrow A^+ + B\cdot + e^-$ (ionization accompanied by formation of a free radical)
$AB \rightarrow AB^*$ (excitation)

These primary reactions are very rapidly followed by secondary reactions:

$$AB^+ + e^- \rightarrow AB^*$$

$$A^+ + e^- \rightarrow A^*$$

The molecules are highly excited, and the energy produced by the secondary reactions is five to six times greater than that required to break down chemical bonds. The molecules can separate to form free radicals:

$$AB^* \rightarrow A\cdot + B\cdot$$

Positive ions, excited molecules, free radicals, and electrons are consequently the energy-rich, reactive radiation products that play a role in subsequent reactions.

Polymers subjected to heavy doses of radiation undergo marked changes. These are due either to degradation brought about by reactions that break down the main chain or to cross-linking with the formation of bridges between chains. Chapiro[1] has classified polymers according to their behavior under irradiation:

Cross-linked polymers	Degraded polymers
Polyethylene	Polyisobutylene
Polypropylene	Poly-α-methylstyrene
Polystyrene	Polymethacrylate
Polyacrylate	Polymethacrylamide
Polyacrylamide	Polyvinylidene chloride
Polyvinyl chloride	Cellulose and its derivatives
Polyvinyl alcohol	Fluoridized polymers
Polyamide	
Polyester	
Polyvinylpyrrolidone	
Rubber (natural and synthetic)	
Polysiloxane	

We see that cross-linking occurs in polymers having a carbon chain in which at least one hydrogen atom is bonded to each carbon atom, and that degradation occurs in polymers made up of units containing a tetra-substituted carbon atom.

Radiation-induced cross-linking of polyethylene has already given birth to a commercially utilizable

†Director, Centre de Recherches de la Soierie et des Industries Textiles, Lyon, France. Paper written originally for *Ciba Rev.*, **1966**(4): 13-19, and reprinted by permission.

process. Cross-linking imparts to this polymer better dielectric properties, gives it greater resistance to hot concentrated acids, and makes it unmeltable. Cross-linked polyethylene undergoes no changes when subjected to a temperature of 125°C for protracted periods, whereas the unmodified polymer melts at 115°C. Similar cross-linking occurs in polypropylene and gives similarly improved properties. Nuclear irradiation in air of synthetic fibers other than polyolefins commonly results in a high degree of degradation, whereas irradiation in a vacuum or in nitrogen leads to cross-linking.[2-7]

Cellulose in the form of wood, wood pulp, filter paper, cotton linters, jute fibers, viscose rayon, or cellulose acetate undergoes rapid degradation when exposed to radiation of more than 1 Mrad in different kinds of atmospheres.[7-12] On the other hand, wool and silk have relatively good resistance to radiation, and the introduction of aromatic groups into wool increases its resistance to gamma rays.[13] The effects of radiation on different types of fiber are shown in Fig. 1.

Gamma radiation is used to sterilize goat hair and combat anthrax. It has proved to be more effective than treatment with formalin.[14]

Radiation is also utilized in sericulture. Male silkworms produce 20 to 30% more silk and are 10 to 15% more viable than females. When exposed to gamma radiation, the male silkworm eggs turn white and the female, black. They can then be sorted mechanically; the male eggs are given preference, with a resulting increase in silk production. Later, gamma rays are used to kill and shrivel the pupae in their cocoons. This results in a higher yield of silk per cocoon and produces filaments with better physical–mechanical properties than those obtained from cocoons dried in the traditional drying cupboards or in autoclaves.[15] Moreover, the filaments are more easily reeled off cocoons treated with radiation than off those treated with hot air. In the Soviet Union, a semi-industrial automatic installation using ^{60}Co (100 thousand curies) treats up to 10 tons of cocoons per day. According to Pancirolli, Murardi, and Svilokos,[16] a minimum dose of 200 thousand rads of gamma radia-

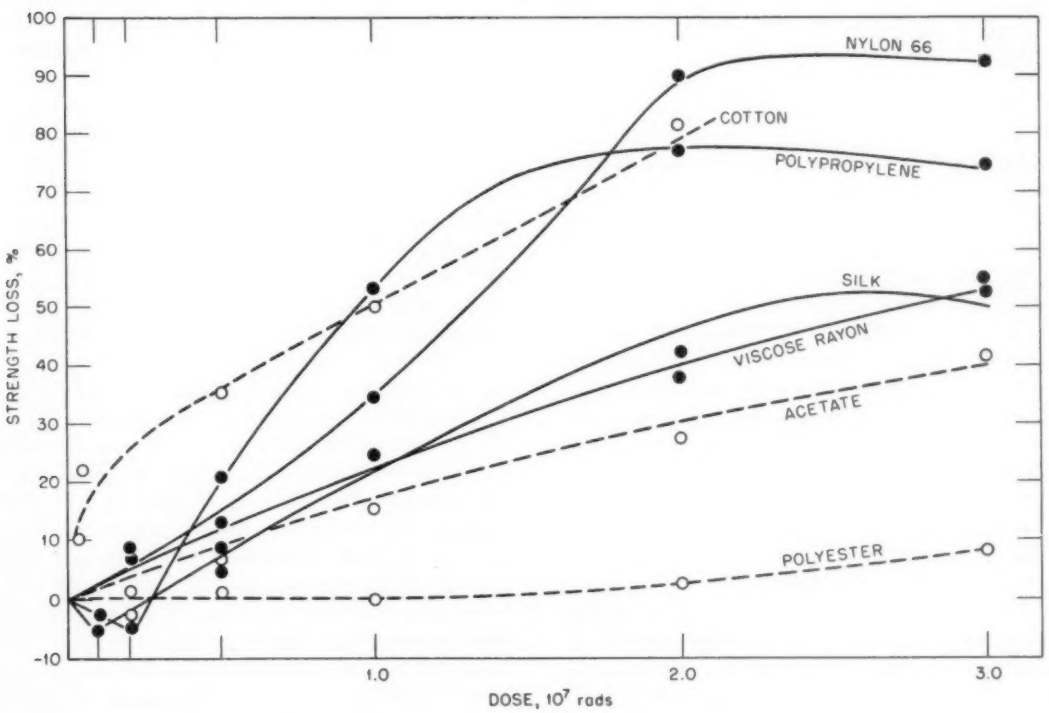
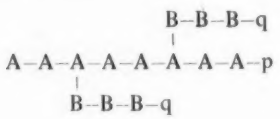


Fig. 1 Effect of nuclear radiation on the strength of various fibers.

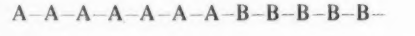
tion is required to kill the pupae in the cocoons of the *Bombyx mori* silkworm.

Graft Copolymerization

The production of graft polymers (graft copolymerization) by high-energy irradiation is a new method developed by Magat and Chapiro,[17] Ballantine, Glines, and Mesrobian,[18] Bevington and Eaves,[19] and their students. Graft polymers have the structure



i.e., in the macromolecule, Ap, the lateral chains, Bq, are chemically linked to the main chain. This peculiarity generally imparts to graft polymers the properties of both polymers, i.e., of Ap and Bq. The production of graft polymers is based on the formation, by the action of high-energy radiation, of "active centers" of a radical nature in the macromolecule. These macro radicals make possible a chemical linkage with a polymerizable monomer, B, which forms the first link in the lateral chain, Bq. Block copolymers with the structure



may be regarded as a special form of graft polymer, the grafted branches being fixed to the ends of the chains. The nature of these copolymers is determined by the structure of the polymers used.

When exposed to radiation, polymers having a hydrogen atom attached to every carbon atom in their main chain undergo mainly rupture of their lateral links (polyethylene, polyvinyl chloride, polyester, etc.) and form graft polymers. Polymers containing tetrasubstituted carbon atoms undergo degradation by destruction of their main chains and form block copolymers. The radiation may be applied in doses too small to have a detrimental effect on the physical–mechanical properties of the material.

Two radiation-grafting (graft copolymerization) techniques are at present in favor:

1. **The use of frozen radicals**: irradiation of the polymers, usually in a vacuum, followed by thermal or photon decomposition of the radicals in the presence of a monomer. The number of radicals obtained is increased by irradiating the polymers at low temperatures.

2. **Direct irradiation**: synthesis of the copolymer by irradiation of the polymer–monomer system. The macro radicals formed in situ take immediate part in the formation of the grafted branches.

After radiation grafting, excess monomers and homopolymerizates are solvent-extracted from the films, fibers, or fabrics.

Radiation grafting is influenced chiefly by the extent to which the polymer is swollen, the radiation dose, the monomer dilution, possibly by the nature of the monomer solvent, and by the radiation sensitivities of the monomer and polymer. According to Armstrong and Rutherford,[7] the results obtained when grafting vinyl monomers onto textile fibers are improved by the presence of traces of water in the vapor phase, but the results are detrimentally affected by oxygen. These two researchers have applied this vinyl-monomer-grafting technique to numerous natural and synthetic fibers, with investigation of the monomers acrylonitrile, vinyl acetate, vinyl crotonate, vinyl propionate, vinyl butyrate, and vinyl methacrylate. *n*-Vinyl pyrrolidone has been grafted onto acrylic fibers,[20,21] acrylamide onto polyamide 66, styrene onto wool and cotton,[22] acrylonitrile onto polyvinyl chloride fibers,[23] and acrylic and methacrylic acids onto polyethylene and polypropylene.[24]

Irradiation of a textile polymer in the presence of a monomer in solution results in a graft far stronger than one obtained in the presence of monomer vapors. Thus, by irradiating pure or cyanoethylated cotton impregnated with an aqueous solution of acrylonitrile and zinc chloride, Arthur, Demint, et al.[25,26] were able to obtain 25% grafts on cyanoethylated cotton with a gamma-radiation dose of 1 Mrad. However, this process is possible only if a polar solvent is used for the acrylonitrile.[27]

Radiation grafting of pure styrene onto cellulose is a heterogeneous reaction in which diffusion of the monomer in the fiber plays a dominant role. According to Huang and Rapson,[28] the graft will "take" only if the cellulose has been impregnated with a polar medium, e.g., water, formamide, formic acid, acetic acid, or dimethyl sulfoxide. The swelling agent facilitates diffusion of the styrene by breaking down the hydrogen bonds and loosening the cellulosic chains. With cotton, 20% water content gives the highest percentage of graft-material take-up. Mercerized cotton behaves similarly except that the amount of material grafted on is doubled. With viscose rayon, the highest take-up of graft material is obtained with a water

content of 60 to 80%, the take-up decreasing above this level (Fig. 2).

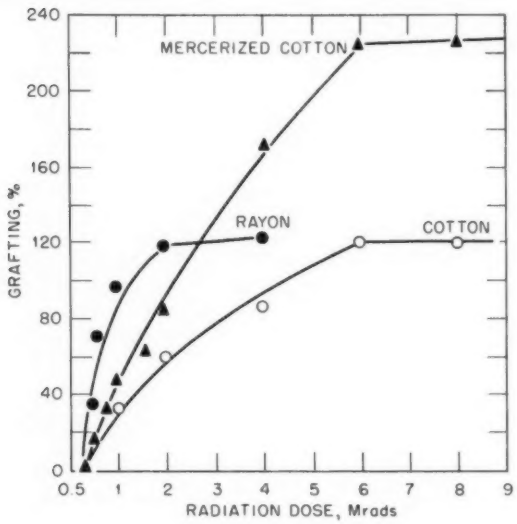


Fig. 2 Grafting of styrene onto cellulose by direct irradiation, showing the effect of increase in radiation dose and of type of cellulose. The water contents of both cottons were 40% and of the viscose rayon, 80%.

Graft copolymerization of vinyl pyridine in solution in methanol onto polyvinyl chloride (PVC) is governed by the gamma-radiation dose used and the diffusion of the monomer in the fiber. According to Roudeix,[29] the amount of vinyl-4-pyridine that will be grafted on varies between 10 and 150%. The new fibers show greater dimensional stability to heat and may be colored with metal-complex dyes of the Cibalan type. Styrene can be grafted onto PVC fibers simply by gamma irradiation of the polyvinyl chloride–styrene system in methanol. The styrene graft improves the electrical resistance of the PVC and its heat stability.[30]

Acrylamide is grafted onto either the surface or into the whole mass of polyamide 66 fibers.[22,31] When a surface graft is required, the polyamide is first exposed to gamma radiation in a nitrogen atmosphere and then immersed in acrylamide in solution in methanol. If the polyamide is irradiated in ordinary air, the graft will take throughout the whole mass of the fiber. Incidentally, it has been established that the speed with which methacrylic acid in aqueous solution grafts onto preirradiated polyamide 66 is proportional to the square root of the duration of radiation exposure.[32,33]

The grafting of styrene onto polyamide 66 fibers has also been investigated.[34-36] The preirradiation technique produces the best results if the polyamide is irradiated in water, dried, and then immersed in a solution of 20% styrene, 65% alcohol, and 15% water (Table 1). Styrene and acrylonitrile radiation grafts improve the water-repellent properties of polyamide fibers. Conversely, it has been established that maleic or acrylic acid radiation grafts onto polyamide appreciably increase the water-absorbing properties of this polymer. Moreover, salt formation by the acid groups with sodium carbonate or calcium acetate gives the copolymer a higher melting point. If all the acid groups are calcified, the melting point is raised to 400°C in the case of polyamide with 20% grafted-on material.[37]

The graft copolymerization of polyvinyl alcohol fibers has been thoroughly studied with the objective of eliminating their sensitivity to water and certain organic solvents. Japanese researchers[38] grafted styrene or methyl methacrylate onto polyvinyl alcohol hydrate films and extracted the homopolymers. Films that had been exposed to gamma radiation in the presence of pure methyl methacrylate increased 40-fold in weight, whereas films irradiated in the presence of pure styrene increased only 10-fold. The amount of material grafted on is lower when polyvinyl alcohol is irradiated in a monomer–acetone–water system. Santo and Gal[39] obtained a 17-fold increase by exposing

Table 1 Comparison of Two Radiation-Grafting Methods Applied to Polyamide 66

Radiation dose, rads	Irradiation method	Percentage of styrene grafted on	Tensile strength, lb/in.	
			Warp	Weft
0		0	89	140
7×10^5	Simultaneous	42	82	100
2×10^6	Simultaneous	95	81	100
2×10^6	Preirradiation	42	100	88

polyvinyl alcohol films to an X-ray dose of 4×10^4 r in the presence of methyl methacrylate in methanol solution.

Other recent studies[40] were conducted with polypropylene fibers. They showed that graft copolymerization produced better results with acrylic acid or methyl methacrylate and gamma irradiation of films, filaments, and fibers of nonoriented polypropylene than with those made of polypropylene oriented by stretching. The speed with which acrylic acid or methyl methacrylate grafts take appears to be determined, in the case of preirradiation in air, by the crystallinity of the various samples, the diffusion speed of the monomer, the content of free radicals, and the number of peroxide and hydroperoxide groups.

Chloromethylstyrene is grafted onto polypropylene fibers[41] to improve their dye affinity and thermal stability, to impart to them antistatic properties, and to make them water-absorbent, all without impairing their mechanical properties.

Radiation grafting of a mixture of monomers onto a textile polymer was also investigated recently.[42,43] Sakurada and his collaborators grafted mixtures of butadiene–styrene, butadiene–acrylonitrile, and styrene–acrylonitrile onto cellulosic and polyvinyl alcohol fibers. In every case, any particular mixture of two monomers resulted in very clearly defined maximum amounts of grafted-on material (Fig. 3).

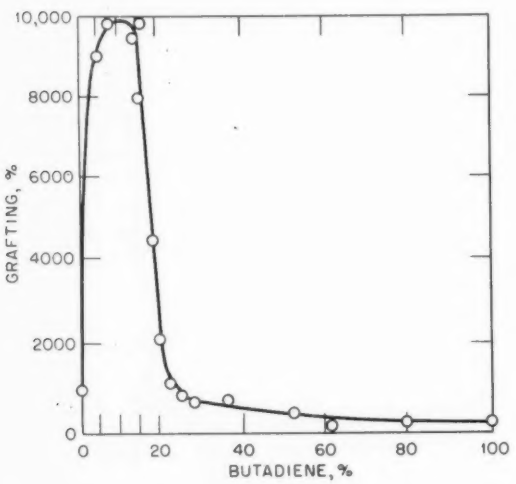


Fig. 3 Grafting of styrene–butadiene onto ordinary viscose rayon. Comonomer concentration about 50%; dose rate 8.5×10^3 rads/hr, total dose 1.4 Mrads; processing temperature 30°C. Grafting is maximum with 10% butadiene and 90% styrene.

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Section
IV
Isotopes and Radiation Technology

Applications in Life Sciences

Possibility of Tumor Therapy with ^{252}Cf Radiation

By Harold L. Atkins*

Abstract: *The possibility of using ^{252}Cf as a source of radiation for tumor therapy is discussed, together with theoretical bases for the suggested advantages of this source.*

It has long been recognized[1] that the presence of oxygen is important in the response of many systems, particularly of mammalian cells, to radiation. The suggestion that lack of oxygen may be a factor in the response of human malignancies to ionizing radiation and, in fact, that radiation resistance associated with anoxia may be the cause of failure to cure many tumors, has aroused the interest of radiation therapists for more than a decade. There have been many attempts to utilize this principle in the treatment of human malignancy with ionizing radiation.

Microscopic examination of many human tumors has shown areas of necrosis due to disorganization in malignant-cell growth, which at times tends to outstrip the blood supply.[2] While the outer rind of a tumor nodule may be well oxygenated, the partial pressure of oxygen rapidly diminishes toward the necrotic core. Some of the still-viable tumor cells exist under conditions of very low oxygen concentration. The sensitivity of cells to ionizing radiation apparently increases rapidly until the oxygen partial pressure reaches about 20 mm Hg (Fig. 1). Further increase of oxygen tension into the range of well-vascularized normal tissue (40 to 100 mm Hg) results in only a small increase in radiation sensitivity.

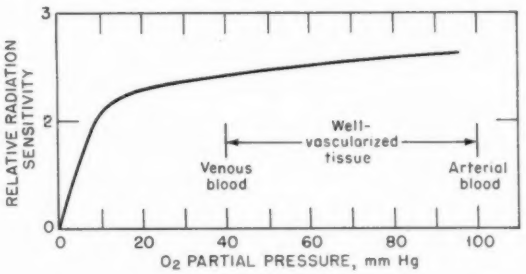

Fig. 1 General curve of relative radiation sensitivity as a function of oxygen partial pressure. This relation has been found to be true for many biological systems.

The conclusion is, therefore, that failure to cure tumors by radiation therapy may be due to the relative radiation resistance of the more centrally placed, partially anoxic, tumor cells. Theoretically, by raising the partial pressure of oxygen in tumors, the cure rate could be improved without substantial increase in normal-tissue reaction.

Several approaches have been used in an attempt to circumvent the problem of radiation resistance of anoxic tumor cells. The most popular approach today is to place the patient in a chamber containing oxygen at 3 to 4 atm pressure and, after allowing suitable time for equilibration, to irradiate the tumor-bearing region. This approach was pioneered by Churchill-Davidson[3,4] at St. Thomas's Hospital, London, in the early 1950's and has been used by many others since.[5-8] Despite extensive use of this method by many investigators, there is no conclusive proof that cure rates have been improved. In addition, the method is rather tedious and requires special equipment and personnel.

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Attempts have been made to improve regional oxygenation by intra-arterial administration of hydrogen peroxide.[9] However, it has not been possible to achieve a substantial increase in oxygen concentration within tumors by this method, and the procedure is not innocuous.

The converse of providing increased oxygen is to deplete the oxygen in normal tissues so that their relative radiation sensitivity is decreased to the level of that of the anoxic cells. This is practical only in special circumstances for peripheral tumors and is also fraught with difficulties and danger if good deoxygenation is not obtained.[10,11]

Another approach to this problem has been receiving close attention in recent years—the use of high-LET (linear-energy-transfer) radiation. The distribution of energy along the ionization track induced by X and gamma rays in tissue is rather diffuse (0.2 to 10 kev/μ), and the biological effects produced usually require two or more "events" in the target volume. When radiation doses are spaced, cells that have had insufficient "hits" may recover between doses. With densely ionizing radiation (LET $>$ 20 kev/μ), each event may be lethal to a cell, and no recovery between doses is apparent.[12,13] The presence of oxygen is then not so important to the biological effect. This is illustrated in Fig. 2, in which the effects of both low (250-kvp X rays) and high (32-Mev alpha particles) LET radiation on survival of human kidney cells in cultures are shown.[14] The curves for irradiation by 250-kvp X rays in air and nitrogen show a "shoulder"

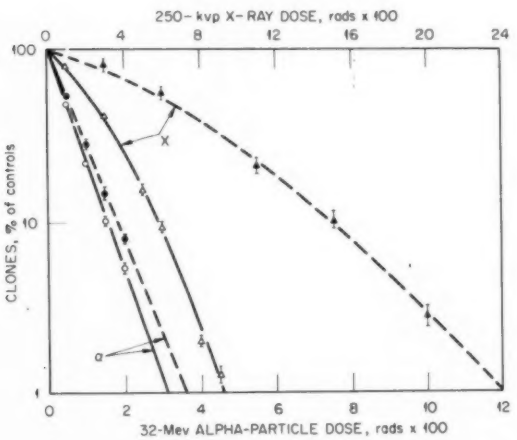


Fig. 2 Effects on survival of cultured human kidney cells of 32-Mev alpha particles and of 250-kvp X rays in air (solid lines) and in nitrogen (dashed lines). From Barendsen.[14]

due to the requirement of more than one hit per target area. The ratio of the dose in nitrogen to that in air to produce the same survival (oxygen enhancement ratio, or OER) is approximately 2.5. The plotted response to the alpha-particle irradiation is a straight line, and the OER is only about 1.2.

Figure 3 illustrates[14] the effect of increasing LET on the oxygen enhancement ratio. Curve 2 shows a

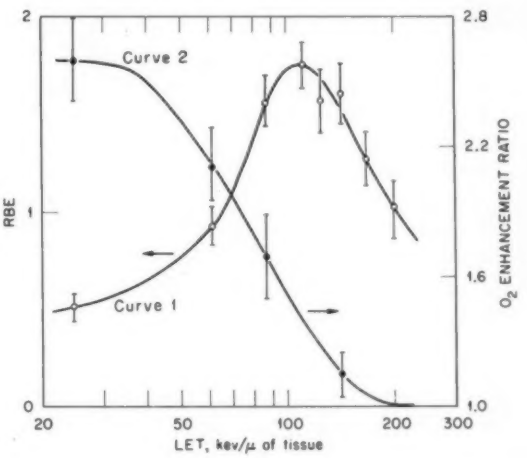


Fig. 3 Relation of LET in unit-density tissue to relative biological effect per unit dose (100 X $1/D_0$) in rads and to oxygen-enhancement ratio. From Barendsen.[14]

maximum OER up to a LET of 40 kev/μ, after which there is a sharp decrease, the minimum being reached at 200 kev/μ. At the same time, the relative biological effect (RBE) increases (curve 1) and reaches a maximum at 110 kev/μ, after which it decreases owing to a saturation effect (overkill).

Several varieties of high-LET radiations are available, but the most practical one at present for clinical purposes is fast neutrons.[15] The higher energy generator- or cyclotron-produced neutrons have a wide range of LET—from 10 to 1000 kev/μ—but are mainly between 10 and 30 kev/μ. Fission-spectrum neutrons are somewhat better,[16] with a LET of 50 to 60 kev/μ. However, the penetration of a beam of fission-spectrum neutrons is inadequate for use on deep-seated tumors.

Cyclotron-produced neutrons were first used by Stone[17,18] in the late 1930's, before much was known about the biological effects of neutrons and such factors as recovery and oxygen enhancement ratios. While effective tumor control was obtained in many

patients, severe late reactions due to overdosage caused abandonment of the project. Renewed interest was evidenced by the group at Hammersmith Hospital, London, in the early 1960's, after better understanding of the biological effects of neutron irradiation became available. Preliminary trials of irradiation of human tumors are under way following preparatory biological experimentation.[19,20] Other investigators are interested in exploring the use of generator-produced neutrons by various reactions,[21-23] but dose rates currently available are insufficient.

Schlea and Stoddard[24] were the first to suggest the use of californium isotopes as implantable fission-neutron sources. Wright and others[25] at the Savannah River Laboratory of the U. S. Atomic Energy Commission developed encapsulated ^{252}Cf sources suitable for interstitial application. While not supplanting all the applications of cyclotron-produced neutrons for tumor therapy, these implantable sources are especially useful for certain applications and have definite advantages over other sources of neutrons.

Californium-252 decays by alpha-particle emission and spontaneous fission. Alpha decay is the controlling factor in the half-life of 2.6 years. Approximately 3.8 neutrons are emitted per fission, and the spectrum is similar[26] to that of ^{235}U fission, with a modal energy of about 1 Mev. Accompanying the fission neutrons are gamma rays due to the fissioning process and the fission-product decay. The gamma dose in rads is approximately 37% of the neutron dose, and the ratio remains constant with time since the decay of the fission products is rather rapid.[27] The fission fragments and alpha particles are readily absorbed in the walls of the platinum–iridium container. The required amounts of ^{252}Cf are so small (microgram quantities are equivalent in radiation effect to milligram amounts of radium) that the material can be electrodeposited on a very thin wire, and thus extreme flexibility in source design is possible (Fig. 4).

A number of advantages of the use of ^{252}Cf are apparent:

1. *Cost:* The current cost of ^{252}Cf is $100 per 0.1 μg, but this may be decreased considerably in the near future as new production programs mature.[28]

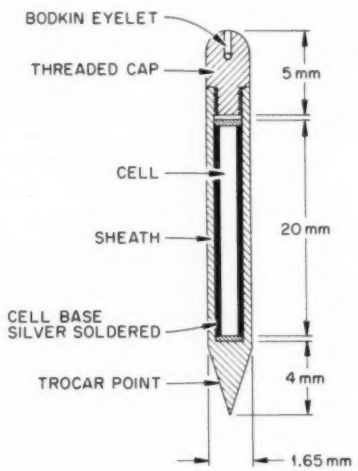
2. *Reliability:* Generators and cyclotrons, in addition to being expensive, are also temperamental. They are not yet in the same stage of reliable operation that deep X-ray and teletherapy units are for day-to-day clinical use. This problem is not associated with the use of ^{252}Cf.

3. *Facility and personnel:* Storage of sources and equipment for application is simple, with no extra personnel being required. Accelerator sources require separate rooms or buildings and the presence of several people for maintenance and operation.

4. *Energy:* Because the fission spectrum has a higher LET, the OER is probably lower than that of neutrons produced by accelerator reactions.

However, because of the need for implantation, only tumors that are accessible can be considered for irradiation with ^{252}Cf, e.g., carcinoma of the uterus (cervix and fundus) and epitheliomas of the oral cavity. The flexibility in source design which is possible with californium may allow treatment of sites that could not be treated with radium or other similar sources. It may also prove preferable in most cases to combine interstitial californium therapy with external beam therapy in order to shorten the uncomfortable period of implantation and to affect the residual nidus of anoxic, radiation-resistant cells remaining after conventional radiation therapy.

Several questions must be answered prior to a therapeutic trial with the californium sources. It is necessary to know the relative biological effects of this



DIMENSIONS, mm	SHEATH	CELL
EXTERNAL LENGTH	30.05	21.00
INTERNAL LENGTH	21.05	20.00
EXTERNAL DIAMETER	1.65	1.00
INTERNAL DIAMETER	1.05	0.60
WALL	0.30	0.20

Fig. 4 Original Savannah River Laboratory ^{252}Cf source for interstitial implantation (Ref. 25). Both sheath and cell of 90% platinum–10% iridium. Later sources have been manufactured to slightly different specifications. Afterloading cells have also been constructed.

form of irradiation as compared to that of more conventional sources such as radium or ^{60}Co. The effect of protracted vs. acute irradiation must be determined, and the tolerance dose for normal tissues must be known.

The distribution of radiation about the californium sources is similar to that of radium, being dependent primarily on the inverse-square-law relations rather than on tissue absorption—at least in the region of greatest interest, which is up to 5 cm from the source. Approximately 37% of the rad (roentgen absorbed dose) dose is due to the associated gamma emission (Fig. 5). However, the preponderance of the biological effect is due to the neutrons because of their high LET.

The presence of a mixed type of emission makes for some complications in predicting biological effects. We have worked with human tumor cells in culture (HeLa-S_3) in order to compare the effect of californium radiation with that of radium and teletherapy apparatus. Our results show that the RBE of californium radiation is about 2.9 times that of protracted irradiation with radium, and about 2.4 times that of acute irradiation with ^{60}Co. These results were obtained with the same type of cells by Hall, Bedford, and Oliver[29] (Fig. 6).

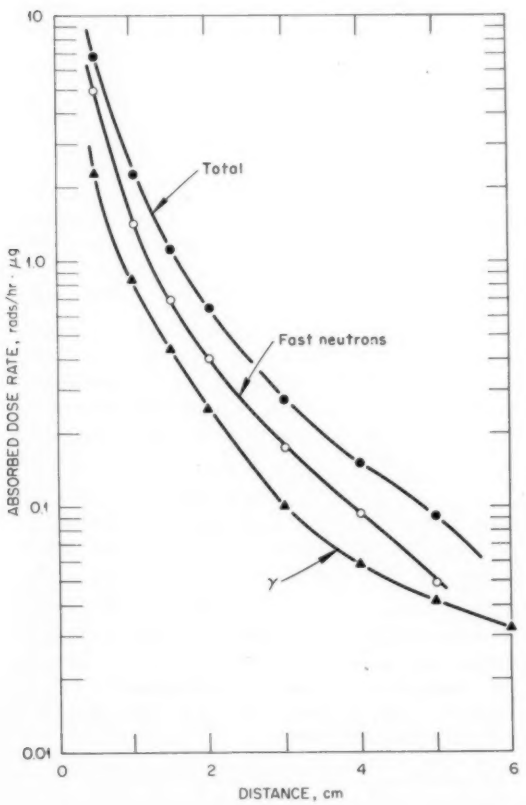


Fig. 5 Distribution in tissue-equivalent phantom of absorbed dose from a ^{252}Cf source.

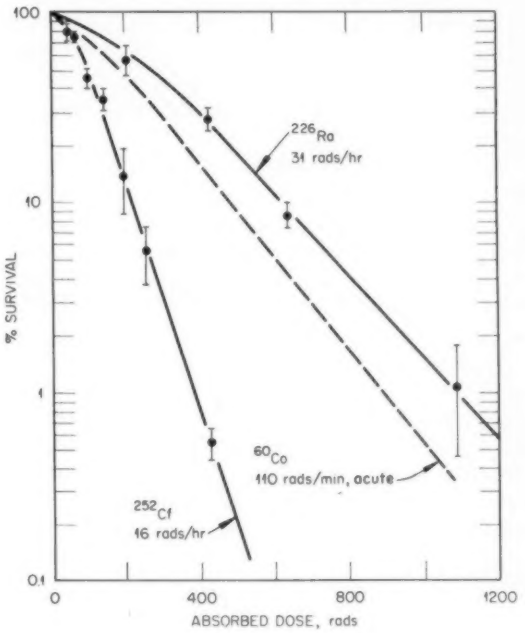


Fig. 6 Effects of ^{252}Cf and ^{226}Ra irradiation on survival of HeLa-S_3 cells. The RBE of the ^{252}Cf is approximately 2.9 relative to the ^{226}Ra. Also shown is the effect of acute irradiation with ^{60}Co gamma rays on the same cell line, taken from Ref. 29.

Of crucial interest is the oxygen enhancement ratio. The OER for acute irradiation (110 rads/min) of HeLa cells with ^{60}Co was found by Hall et al. to be 2.6, whereas for protracted irradiation with ^{60}Co (32 rads/hr) it was only 1.5. This was due to the results under anoxia being nearly the same for the two rates of irradiation, while the RBE for the acute irradiation under aerobic conditions was approximately 1.4 with respect to protracted irradiation.

We are now in the process of determining the OER for californium. Unfortunately, this is rather time-consuming since only one culture can be irradiated at a time with the limited supply of californium now available. It is to be hoped that the combination of protraction along with high LET radiation will result in

a very low OER, perhaps 1.1 or 1.2. If so, this would certainly indicate[30] a marked advantage in the use of californium over conventional sources for radiation therapy, and even over accelerator-produced fast neutrons with an OER of 1.5.

In addition to determining the effects on tissue cultures, we are also evaluating the effect of californium on pigskin with respect to a maximum tolerable dose (moist desquamation with subsequent healing). Following this it should be possible to begin irradiation of patients with certain malignancies to determine the efficacy of californium under clinical conditions.

However, it will take many years to evaluate whether any advantage exists in the use of ^{252}Cf in clinical situations. Because the oxygenation of tumors may improve when radiation is applied in small fractions and as the size of tumor nodules decreases during the course of therapy, the oxygen effect may not be quite so important as previously thought.[31,32] Undoubtedly, a proportion of cells in many tumors may remain anoxic throughout a course of radiation therapy, but the effect may be small and difficult to detect. With the coming abundance of ^{252}Cf for medical use, it is hoped that cooperative programs among a number of clinical centers will allow the answer to this important question to be found sooner than would otherwise be possible. (MG)

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Survey of the Use of Radionuclides in Medicine

By K. D. Williams and J. D. Sutton*

Abstract. *The results of the first phase of a survey on the use of radionuclides in medicine in the United States are reported.*

"Nuclear medicine is the scientific and clinical discipline concerned with the diagnostic, therapeutic (exclusive of sealed radiation sources), and investigative use of radionuclides."[1] A survey of this field, including the use of sealed sources, is being conducted by the National Center for Radiological Health (NCRH). The overall objectives of the study are to provide statistically valid information on the uses of radionuclides in nuclear medicine and to design a system for collecting similar information on a continuing basis. The results are expected to aid in identifying possible problem areas and in developing techniques to minimize radiation exposure to the human population.

Phase I of the three-part study is a national survey of all licensed and/or registered medical users of radionuclides, i.e., physicians who have obtained licenses from either the U. S. Atomic Energy Commission (AEC) or an Agreement State to use radioactive materials in their practice and/or physicians required by state radiation-control programs to register non-AEC-controlled radioactive materials. Phase II will be a qualitative study of radiopharmaceutical testing and manipulation, patient preparation, and instrumentation in the practice of nuclear medicine. Phase III is the design of methodology for maintaining up-to-date statistical data on the use of radionuclides in medicine.

Method of Conducting Survey

Physician Registry

The mailing list for the Phase I survey contained the names and addresses of 7024 physicians in the United States licensed and/or registered to administer radionuclides to humans. As of Sept. 30, 1966, the AEC and Agreement State programs reported 5028 "by-product material" licensees for medical use. However, the number of licensed physicians exceeds the number of licenses since physicians may practice under a specific, general, broad, or institutional license, and the latter two types apply to groups of physicians rather than individuals. Also, the users of radium and accelerator-produced radionuclides were estimated to be approximately 200 as of July 1966. Computer methods were used to eliminate duplicate names, i.e., those of physicians that appeared on more than one list.

Questionnaire

A questionnaire that included a listing of the more common diagnostic and therapeutic procedures was

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designed by Stanford Research Institute (SRI). For each procedure, three checkoff blocks were provided: the first to be checked by physicians licensed to perform the procedure, the second by those who had ever used the procedure, and the third by those who had *not* used it in the past year (1966). Spaces were provided for entering the numbers of patients and administrations for the year for each procedure and for information on procedures not listed. Procedures were listed in two categories:

1. Diagnostic procedures
   - Function studies: routine patient counting and sample counting
   - Scanning studies: pictorial representations of isotope distribution
   - Research: nonroutine investigative studies
2. Therapeutic procedures
   - Radiopharmaceutical therapy: internal administration of radiopharmaceuticals
   - Brachytherapy: use of sealed or encapsulated sources for interstitial, superficial, or intracavitary procedures
   - Teletherapy: ^{60}Co or ^{137}Cs beam therapy
   - Research: nonroutine investigative procedures

Response

By the end of January 1967, questionnaires had been sent to all the physicians on the mailing list. There was a 40% return during the next 2 months, and an additional mailing of the same questionnaire increased the number of returns to about 54% by the end of June. The respondents, grouped according to type of practice, were:

	Number	Percent
Physicians actively using radionuclides	2510	65.1
Physicians not actively using radionuclides	691	17.9
Physicians included in another response	416	10.8
Nonpractitioners	165	4.3
Retired physicians	35	0.9
Deceased (answered by another physician)	31	0.8
Refusals to answer questionnaire	8	0.2
Total	3856	100.0

Physicians Actively Using Radionuclides

Of the 2510 responding physicians actively using radionuclides, 1713 were classified as performing primarily* diagnostic studies, 678 primarily* therapeutic studies, and 119 both diagnostic and therapeutic studies (Table 1).

Nine physicians reported more than 10,000 patients each annually. Eight of these had performed large numbers of in vitro triiodothyronine (T-3) binding procedures with ^{125}I or ^{131}I. Four of the eight were practicing in large general hospitals, three worked in clinical laboratories in which the T-3 test was the major procedure reported, and one worked in a clinic with thyroid function, scanning, and therapy procedures. The ninth physician, also in a clinic, reported ^{60}Co teletherapy as his primary procedure.

Forty-two percent of the physicians had yearly patient loads of 100 to 999. Over 90% of those practicing primarily brachytherapy had fewer than 100 patients per year; this is the only type of clinical practice in which a very small number of patients is the rule.

Few respondents were engaged primarily in research, but many of those practicing primarily clinical nuclear medicine were also engaged in research activities. Also, many researchers who did not respond for themselves were included in another's response and therefore were not classified in the category of primary research.

Physicians Not Actively Using Radionuclides

Eighteen percent of the respondents reported that they had not used radionuclides during the year 1966. Since a large percentage of physicians who practice brachytherapy reported very small numbers of patients, it is possible that a large proportion of the responding nonusers are physicians who possess radium and have at some time in the past practiced brachytherapy.

Physicians Included in Another Response

When two or more physicians were in group practice, usually one of them responded for the entire group. Since no estimate of the individual practice could be made, the procedures performed by all

*When a physician reported using both diagnostic and therapeutic procedures but one type of procedure was at least twice the number in the other category, he was listed as being primarily in the predominant category.

Table 1 Classification of Physicians by Primary Practice and Patient Load

Primary type of practice	Responding physicians: Total number of patients per year: Under 10	10 to 99	100 to 999	1000 to 9999	Over 10,000	Total	Percent: Sub-category	Category
Diagnostic studies								
Function	28	259	587	272	8	1154	67.4	
Scanning	15	10	47	15	0	87	5.0	
Mixed function and scanning	1	23	163	169	0	356	20.8	
Research	39	57	19	1	0	116	6.8	
	83	349	816	457	8	1713	100.0	68.2
Therapeutic studies								
Radiopharmaceutical therapy	34	22	1	0	0	57	8.4	
Brachytherapy	192	193	25	1	0	411	60.6	
Teletherapy	1	19	140	19	1	180	26.5	
Mixed therapy	3	10	11	0	0	24	3.5	
Research	3	2	1	0	0	6	1.0	
	233	246	178	20	1	678	100.0	27.0
Mixed diagnostic and therapeutic studies	5	36	61	17	0	119	100.0	4.8
Total users reporting	321	631	1055	494	9	2510		100.0
Percent	12.8	25.1	42.0	19.7	0.4	100.0		

members of the group were included and tabulated as part of the respondent's procedures.

Nonpractitioners

A substantial number of nonphysicians are listed in AEC files in medical or quasi-medical categories, e.g., radiation safety officers who perform calibration and safety work in medical centers and are custodians of radioactive materials. Physicians or veterinarians who use radioactive materials in research on animals or on tissues in medical centers must also have a valid AEC license, but none of these licensees is a medical user of isotopes on humans within the meaning of that term in this study.

Other Categories

The other categories in the above tabulation are self-explanatory.

Results

The replies to the questionnaire with regard to diagnostic procedures are tabulated in Table 2, and therapy in Table 3.

In Vitro Procedures

Three nuclear medical procedures are routinely performed in vitro. These tests are available to all doctors, hospitals, and clinical laboratories without the need for an AEC license. Since only physicians having an AEC or Agreement State license were queried, the number of such tests performed is considerably larger than the number reported here. Nevertheless, the number of these tests performed in 1966 exceeds the total number of all other radionuclide function studies performed.

This use of in vitro studies can be a major factor in minimizing radiation exposure to patients, and other tests based on in vitro studies are being developed.

Function Procedures

One of the first function studies performed in clinical medicine with radionuclides was the study of thyroid physiology using ^{131}I, and this test has been widely used since its inception. It was the most used function study reported in the survey, the number of administrations for this procedure representing more than half of the total administrations for the 50

Table 2 Principal Nuclear Medical Diagnostic Procedures Performed During 1966

Radionuclide	Compound	Procedure	Physicians licensed for procedure	Physicians performing procedure	Patients	
					Number	Percent
		In vitro				
^{131}I or ^{125}I	Triiodothyronine	T-3 binding	1,380	1,066	582,807	99.6
^{131}I	Thyroxine	T-4 resin uptake	3	2	1,124	0.2
^{59}Fe	Resin sponge	Iron binding	15	13	1,261	0.2
					585,192	100.0
		Function				
^{131}I	Sodium iodide	Thyroid uptake	1,527	1,284	301,052	57.2
^{131}I or ^{125}I	Labeled albumin	Blood volume	1,381	908	101,994	19.4
^{131}I or ^{125}I	Sodium iodohippurate	Renal function	817	388	33,245	6.3
^{57}Co	Labeled vitamin B_{12}	Vitamin B_{12} absorption	952	582	24,996	4.7
^{51}Cr	Sodium chromate	Blood volume	1,064	437	22,468	4.3
^{60}Co	Labeled vitamin B_{12}	Vitamin B_{12} absorption	1,149	556	16,486	3.1
^{131}I or ^{125}I	Labeled fats	Fat malabsorption	1,054	505	7,742	1.5
^{51}Cr	Sodium chromate	RBC survival	1,110	604	6,530	1.2
^{59}Fe	Chloride or citrate	Iron turnover	836	287	3,139	0.6
^{131}I or ^{125}I	Labeled albumin	Cardiac output	627	79	1,503	0.3
^{131}I or ^{125}I	Rose Bengal	Hepatic function	33	23	1,202	0.2
					520,357	98.8
39 other procedures with less than 1,000 administrations					6,119	1.2
					526,476	100.0
		Scanning				
^{131}I	Sodium iodide	Thyroid scanning	1,092	908	153,089	37.5
^{99m}Tc	Pertechnetate	Brain scanning	528	330	63,078	15.4
^{198}Au	Colloidal gold	Liver scanning	730	539	41,855	10.2
^{203}Hg	Labeled mercurials	Brain scanning	329	320	37,746	9.2
^{131}I	Labeled albumin (MAA)	Lung scanning	757	562	22,840	5.6
^{131}I	Rose Bengal	Liver scanning	823	503	19,721	4.8
^{197}Hg	Labeled mercurials	Brain scanning	162	145	18,489	4.5
^{203}Hg	Labeled mercurials	Kidney scanning	787	543	16,223	4.0
^{197}Hg	Labeled mercurials	Kidney scanning	646	282	6,972	1.7
^{85}Sr	Nitrate or chloride	Bone scanning	582	398	6,232	1.5
^{99m}Tc	Technetium sulfur colloid	Liver scanning	202	55	4,911	1.2
^{131}I or ^{125}I	Labeled albumin	Placenta scanning	619	325	3,921	1.0
^{131}I	Labeled albumin	Brain scanning	37	34	3,511	0.9
^{131}I	Sodium iodohippurate	Kidney scanning	483	99	2,091	0.5
^{75}Se	Selenomethionine	Pancreas scanning	263	121	1,635	0.4
^{51}Cr	Heat-treated RBC	Spleen scanning	554	287	1,628	0.4
^{125}I	Sodium iodide	Thyroid scanning	5	4	1,354	0.3
^{131}I	Labeled albumin	Heart scanning	69	65	546	0.1
^{87m}Sr	Nitrate or chloride	Bone scanning	130	22	438	0.1
^{197}Hg	Mercurihydroxypropane	Spleen scanning	247	57	389	0.1
^{131}I	Labeled albumin (MAA)	Liver scanning	9	4	311	
^{99m}Tc	Pertechnetate	Thyroid scanning	5	5	259	0.2
^{99m}Tc	Labeled albumin	Placenta scanning	12	12	254	
^{99m}Tc	Labeled albumin	Lung scanning	1	1	200	
					407,693	99.6
25 other procedures with less than 200 administrations					1,768	0.4
					409,461	100.0

Table 3 Principal Therapy Procedures Performed During 1966

Radionuclide	Compound	Treatment	Physicians licensed for procedure	Physicians performing procedure	Patient administrations	
					Number	Percent
		Radiopharmaceutical				
^{131}I	Sodium iodide	Hyperthyroidism	1,229	1,042	20,717	61.4
^{32}P	Soluble phosphate	Polycythemia vera	1,086	581	3,405	10.1
^{131}I	Sodium iodide	Thyroid ablation	869	295	2,316	6.9
^{32}P	Colloidal phosphate	Malignant effusions	724	316	2,033	6.0
^{131}I	Sodium iodide	Thyroid cancer	907	334	1,768	5.2
^{32}P	Soluble phosphate	Leukemia	819	132	933	2.8
^{131}I	Sodium iodide	Cardiac dysfunction	825	224	927	2.7
^{198}Au	Colloidal gold	Malignant effusions	681	152	732	2.2
^{32}P	Soluble phosphate	Osseous metastases	50	41	701	2.1
					33,532	99.4
8 other procedures with less than 100 administrations					211	0.6
					33,743	100.0
		Brachytherapy				
^{226}Ra	Sealed sources	Intracavitary Rx of cancer	734	543	15,700	31.6
^{90}Sr	Eye applicator	Ophthalmic treatment	483	295	11,785	23.7
^{226}Ra	Plaques and moulds	Dermatological treatment	378	109	5,582	11.2
^{226}Ra	Needles	Interstitial Rx of cancer	604	276	4,152	8.4
^{222}Rn	Seeds	Interstitial Rx of cancer	436	158	3,069	6.2
^{60}Co	Needles or seeds	Intracavitary Rx of cancer	283	90	2,737	5.5
^{226}Ra	Nasopharyngeal applicator	Intracavitary Rx of cancer	306	50	2,457	5.0
^{90}Sr	Plaques	Dermatological treatment	8	7	1,182	2.4
^{90}Sr	Nasopharyngeal applicator	Nonmalignant conditions	6	6	678	1.4
^{137}Cs	Sealed sources	Intracavitary Rx of cancer	22	16	548	1.1
^{60}Co	Needles, wire, etc.	Interstitial Rx of cancer	258	31	547	1.1
^{192}Ir	Seeds—nylon ribbon	Interstitial Rx of cancer	51	32	404	0.8
^{226}Ra	Nasopharyngeal applicator	Nonmalignant conditions	18	12	383	0.8
^{198}Au	Seeds	Interstitial Rx of cancer	20	12	106	0.2
^{226}Ra	Eye applicator	Ophthalmic treatment	7	6	100	0.2
					49,430	99.6
9 other procedures with less than 100 administrations					192	0.4
					49,622	100.0
		Teletherapy				
^{60}Co	Beam therapy	524	399	153,714	1,859,845	97
^{137}Cs	Beam therapy	76	25	3,364	60,103	3
				157,078	1,919,948	100

different function studies reported in 1966. The use of radioactive iodine for thyroid studies is a consequence of iodine's unique position in thyroid physiology. Its suitability for tagging other compounds has also led to its use in five other popular procedures. Iodine-131 is the isotope used in more than 85% of the total number of administrations for function studies.

Blood-volume determination is the second most widely used function study. It is predominantly performed with ^{131}I-labeled albumin, although sodium (^{51}Cr) chromate is used in about 1/6 of the studies. The emergence of blood-volume determinations as a significant clinical tool is highlighted by its more than threefold increase in use since 1959 compared to less

than a doubling in frequency of thyroid uptake studies. Accurate measurement of the circulating blood volume is often an important factor in successful management of a surgical patient.

The second most widely used isotope in function studies is ^{57}Co for vitamin B_{12} absorption tests. It is used with a 50% greater frequency than ^{60}Co. The ^{57}Co isotopic form is preferable because of its short half-life and greater counting efficiency with most detectors. In a study[2] conducted by SRI in 1959, ^{57}Co was not reported and ^{60}Co was the major isotope used for vitamin B_{12} studies. The change to ^{57}Co as the predominantly used isotope demonstrates the changing state of the art of nuclear medicine and the trend toward use of isotopes that minimize hazard to the patient.

Scanning Procedures

Radioisotope scanning is most widely used as an aid in diagnosing and managing thyroid diseases. During the last decade, scanning has been significantly extended to the study of other body organs owing to the development of new radioactive tracer agents and improvements in instrumentation. The relative frequency of organ scanning reported is

Thyroid	37.8%	Kidney	6.2%
Brain	30.0	Lung	5.6
Liver	16.3	Other	4.1

Four different radionuclides were reported for brain scanning (Table 4). Radioiodinated (^{131}I) human serum albumin was at one time the most widely used substance, but an improved scanning agent, ^{203}Hg-labeled Chlormerodrin, was rapidly accepted as a clinically useful agent after its introduction in 1960. Because of the relatively high radiation dose to the kidney from ^{203}Hg, Chlormerodrin labeled with ^{197}Hg has been prepared. This isotope decreases the kidney dose significantly, but its short half-life and invariable contamination with ^{203}Hg detract from its usefulness. The radionuclide most used recently in brain scanning, ^{99m}Tc, was introduced in 1964. Its marked advantage over the previously mentioned isotopes in detecting brain tumors is attested to by its frequency of use in 1966, when it surpassed, in number of administrations, all other isotopes used in brain scanning.

Colloidal ^{198}Au and ^{131}I-labeled Rose Bengal were used for more than 90% of the liver-scanning administrations reported. The ^{131}I compound yields less radiation exposure to the patient but gives less uniformity of the uptake pattern. The recently introduced ^{99m}Tc-labeled sulfur colloid is useful because of its emission of a monoenergetic gamma ray, its short half-life, its economy, and its convenient availability. Also reported was ^{131}I-microaggregated human serum albumin. It also yields less radiation exposure to the patient than the two isotopes most commonly used for liver scanning.

Radiopharmaceutical Therapy

Of the reported radiopharmaceutical administrations, 3.5% were for therapy, with diagnosis accounting for 96.5%. Internally administered ^{131}I for treatment of hyperthyroidism accounted for 74% of the total number of therapeutic administrations of this radionuclide reported in the survey.

Brachytherapy

Of the seven radionuclides listed for brachytherapy use, radium accounted for 58% of the total number of treatments. As stated earlier, the number reported is less than the number administered because radium can be used without a license.

Table 4 Frequency of Radionuclides Used in Organ Scanning

	Percent							
Radionuclide	Bone	Brain	Kidney	Liver	Lung	Placenta	Spleen	Thyroid
^{198}Au	–	–	–	63	–	–	1	
^{51}Cr	–	–	–	–	–	4	78	
^{197}Hg	–	15	28	–	–	–	18	
^{203}Hg	–	31	64	–	–	–	1	
^{131}I	–	3	8	30	99	90	–	100
^{85}Sr	93							
^{87m}Sr	7							
^{99m}Tc	–	51	–	7	1	6	2	

Table 5 Principal Research Studies Performed During 1966

Radionuclide	Compound	Study (as reported in survey questionnaire)	Physicians performing procedure	Administrations	
				Number	Percent
^{131}I	Labeled hormones	Metabolic	14	2,679	16.3
^{3}H and ^{14}C	Labeled aldosterone	Metabolic	4	922	5.6
^{131}I	Labeled albumin	Blood volume	8	752	4.6
^{14}C	Labeled cholesterol	Metabolic	7	408	2.5
^{14}C	Labeled steroids	Metabolic	6	352	2.1
^{3}H	Labeled cholesterol	Metabolic	5	346	2.1
^{3}H	Labeled aldosterone	Adrenal secretion	12	324	2.0
^{133}Xe	Saline solution	Blood flow	5	313	1.9
^{99m}Tc	Labeled albumin	Lung scanning	5	313	1.9
^{85}Kr	Gas	Brain blood flow	4	298	1.8
^{133}Xe	Gas	Muscle blood flow	6	290	1.8
^{85}Kr	Saline solution	Cardiac output	7	289	1.8
^{3}H	Labeled thymidine	Autoradiography	3	280	1.7
^{59}Fe	Ferric chloride	Iron absorption	4	274	1.7
^{131}I	Labeled albumin (MAA)	Lung scanning	5	256	1.6
^{14}C	Labeled cortisol	Plasma clearance	8	227	1.4
^{47}Ca	Calcium chloride	Metabolic	10	218	1.3
^{113m}In	Iron complex	Lung scanning	4	211	1.3
^{3}H	Labeled steroids	Metabolic	2	206	1.3
^{131}I	Labeled human FSH*	Radioimmunoassay	1	200	1.2
^{99m}Tc	Labeled albumin	Heart scanning	5	200	1.2
				9,358	57.1
289 other procedures with less than 200 therapeutic research procedures				6,869	41.8
				181	1.1
				16,408	100.0

*Follicle-stimulating hormone.

Table 6 Principal Radionuclides Used in Diagnostic Research Studies Performed During 1966

Patient administrations			Patient administrations		
Radionuclide	Number	Percent	Radionuclide	Number	Percent
^{131}I and ^{125}I	5,825	35.8	^{18}F	114	0.7
^{3}H	3,315	20.4	^{24}Na	113	0.7
^{14}C	1,854	11.4	^{132}I	100	0.6
^{99m}Tc	827	5.1	^{32}P	92	0.6
^{85}Kr	620	3.8	^{137m}Ba	85	0.5
^{133}Xe	603	3.7	^{57}Co	68	0.4
^{51}Cr	490	3.0	^{198}Au	45	0.3
^{47}Ca	364	2.2	^{64}Cu	42	0.3
^{75}Se	349	2.1	^{45}Ca	31	0.2
^{59}Fe	277	1.7	^{131}Cs	30	0.2
^{113m}In	211	1.3	^{95}Zr	25	0.2
^{42}K	203	1.3	^{28}Mg	20	0.1
^{35}S	171	1.1	^{55}Fe	18	0.1
^{22}Na	163	1.0	^{60}Co	15	0.1
^{85}Sr	125	0.8	^{197}Hg	15	0.1
				16,210	99.8
			5 other radionuclides	17	0.2
				16,227	100.0

Teletherapy

A total of 157,078 patients were reported as receiving a total of 1,919,948 teletherapy administrations in 1966, an average of about 12 administrations per patient. Cancer was the only condition reported as treated by teletherapy. The only radionuclides used were ^{60}Co and ^{137}Cs, with 97% of the treatments being made with ^{60}Co.

Research

Three times as many research studies (Table 5) were reported as the total number of clinical studies for function, scanning, and therapy. The frequency of use of the 30 principal radionuclides reported for diagnostic research is shown in Table 6. Four of these—^{131}I, ^{125}I, ^{14}C, and ^{3}H—were used in 67% of the studies.

Predictions

The total number of radionuclides, exclusive of brachytherapy and teletherapy, showed a fourfold increase in the 7-year period from 1959 to 1966, i.e., from 400,000 to 1,743,000. The data are presented in Table 7.

Table 7 Comparison Between the 1959 and 1966 Studies by Principal Radionuclides

Radionuclide and use	Percent 1959	Percent 1966
^{125}I and ^{131}I		
Diagnosis		
Thyroid	66.5	44.2
Blood volume	5.5	9.9
Fat studies	2.8	0.7
Kidney	1.2	3.4
Liver	1.0	2.1
Lung	–	2.2
Tumor	0.8	–
Other	0.4	1.4
Therapy		
Hyperthyroid	4.1	2.0
Cardiac	0.9	0.1
Thyroid cancer	0.3	0.3
Other	1.8	0.2
	85.3	66.5
^{32}P		
Diagnosis	0.4	0.1
Therapy		
Leukemia	2.7	0.1
Other	1.3	0.4
	4.4	0.6
^{60}Co		
Diagnosis	3.1	1.6
Therapy	0.5*	0.3*
	3.6	1.9
^{198}Au		
Diagnosis	0.1	4.1
Therapy	0.5	0.1
	0.6	4.2
^{51}Cr		
Diagnosis		
Blood volume	2.9	2.2
Other	0.1	0.9
	3.0	3.1
^{59}Fe		
Diagnosis	0.2	0.3
^{90}Sr		
Therapy	0.6	1.3
^{42}K		
Diagnosis	0.2	–
^{82}Br		
Diagnosis	0.3	–
^{57}Co		
Diagnosis	–	2.5
^{3}H		
Diagnosis	0.3	0.3
^{14}C		
Diagnosis	–	0.2
^{99m}Tc		
Diagnosis	–	6.7
^{203}Hg		
Diagnosis	–	5.2
^{197}Hg		
Diagnosis	–	2.6
^{75}Se		
Diagnosis	–	0.2
Other	1.5	4.4
Total	100.0	100.0

*Does not include ^{60}Co teletherapy administrations.

Table 8 Survey Findings and Projections of the Use of Radionuclides in Medicine During 1966

Use	Reported by 54% of survey population		Projection for total population	
	Patients	Administrations	Patients	Administrations
Function studies				
In vitro	585,192	-	1,035,000	
In vivo	497,854	526,476	882,000	930,000
Scanning studies	389,706	409,281	690,000	725,000
Diagnostic research	13,621	15,943	24,100	28,300
Radiopharmaceutical therapy	28,664	33,743	50,700	59,500
Brachytherapy	31,053	49,622	55,000	87,800
Teletherapy	157,078	1,919,948	278,000	3,390,000
Therapy research	90	181	160	320
Total	1,703,258	2,955,194	3,015,000	5,221,000

The preliminary findings from the survey together with projections to the total population—i.e., to the total including the 46% of the doctors who did not respond to the questionnaire—are summarized in Table 8. (MG)

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1. M. A. Bender, Editorial, *J. Nucl. Med.* 8: 901 (1967).
2. R. R. Tarrice and M. S. Blumberg, Radioisotopes in Medicine, USAEC Report SRIA-13, Stanford Research Institute, December 1959.

ROLE OF COMPUTERS IN RADIOTHERAPY
Report of Panel, Vienna, 1967
IAEA, Vienna (STI/PUB/203)

Twenty-two persons, from six countries as well as from the International Atomic Energy Agency and the World Health Organization, attended a second* panel meeting on uses of computers in radiation therapy. The record of the meeting contains the 13-member panel's summary of discussion and recommendations on the computer's role in this field. Seventeen working papers prepared in advance were available before the meeting and are included in the record. Computers are currently used in external-beam and in interstitial and intracavitary radiation therapy more than in any other applications. However, their usage in record keeping and data analysis and in automation of treatment and auxiliary equipment, although now small, is expected to increase in the next few years. Little attention has been given to their use in systems analysis of the overall operations of a radiation-therapy center. (MG)

*The report of the first panel, which met in Vienna in 1965, was published by the IAEA as Technical Report No. 57, *The Use of Computers for Calculation of Dose Distributions in Radiotherapy*.

*RADIOISOTOPES IN MEDICINE: IN VITRO STUDIES**

On Nov. 13–16, 1967, Oak Ridge Associated Universities held its 11th symposium on nuclear medicine. Three hundred participants, representing 12 countries, attended. Papers were presented on three different types of in vitro analysis: Protein-Binding Studies and Radioassay, Activation Analysis, and Cytologic and Chromosomal Labeling. The great interest in this subject is indicated by the necessity for a second printing 2 months after the first one was released.

Assay procedures that were discussed involved the use of protein binders of a substrate to be assayed (usually plasmatic), with separation of bound and unbound fractions. One such procedure, the triiodothyronine-binding test, has been widely accepted and in many centers has largely replaced the routine clinical radioiodine thyroid-uptake procedure. There was some discussion of the bases of this test. Measurements of serum thyroxine levels, using ^{125}I- or ^{131}I-labeled compounds as tracers, were discussed; these will undoubtedly tend to replace the protein-bound iodine test. When the binders used are immune proteins, the test is frequently referred to as a "radioimmunoassay." Some of the tests in this category that were described are those for luteinizing and follicle-stimulating hormones in human serum, for human thyrotropin, for parathyroid hormone, and for ACTH.

Activation analysis is gradually working its way into clinical medicine. One promising application—administration of a tracer amount of a stable isotope with subsequent in vitro activation—has the advantage that kinetic studies may be made without injecting any radioactive materials into the patient. The basic principles and methodology of activation analysis are discussed in the proceedings, and potential applications in clinical medicine are suggested. Papers are also included on determination of various specific elements by this technique and on the availability of neutron sources—reactor, machine, and the transuranium radioisotopes (specifically ^{252}Cf)—for use in the activation.

The use of autoradiography in cytology and chromosome studies is particularly interesting since it requires no electronic equipment. Autoradiography, although not yet a routine clinical technique, is a promising one, e.g., for histocompatibility tests in tissue transplantation studies. In work reported in half a score of papers on this subject, the radioisotopes ^{14}C, ^{3}H, ^{125}I, and ^{131}I were used for labeling the biochemical compounds traced. Techniques for high-resolution autoradiography and electron-microscope autoradiography are also discussed. [See also reviews of two books on autoradiography, *Isotopes and Radiation Technology*, 6(2): 210 (Winter 1968–1969).]

The proceedings of the symposium are intrinsically interesting and useful. The good editing and pleasing format in which they are presented enhance their readability. (MG)

*R. L. Hayes, F. A. Goswitz, B. E. Pearson Murphy, and E. B. Anderson (Eds.), *Radioisotopes in Medicine: In Vitro Studies*, Oak Ridge, Tenn., Nov. 13–16, 1967, AEC Symposium Series, No. 13 (CONF-671111), Oak Ridge, Tenn., 1968. (CFSTI, $3.00)

Section

V

Isotopes and Radiation Technology

Safety

Are the Regulations Out To Get Me?*

By William A. Brobst†

Abstract: *New regulations by the Department of Transportation for the transportation of radioactive materials and interpretations which have come out of the development of these regulations are reviewed. Also discussed are special permits and their issuance, future changes, incorporation of IAEA criteria throughout the regulations, acceptable closure devices, enforcement of regulations, etc.*

You will note in the program that my talk is entitled "The High Cost of Red Tape." This is the paper that will be published in the Symposium Proceedings.[1] That being the case, perhaps our time might be better spent if I just refer you to that paper for what it is worth and discuss with you some of the minor but irritating problems you have faced in the last few months in trying to get ready to live with the new regulations. In the published paper I discuss some of the methods you might pursue in trying to cut your costs of getting administrative approvals—special permits—for packages. In that paper I cover such things as the cost to the taxpayer of issuing a special permit, the waste of seldom-used casks, the desire for each project manager to have his own shining stainless-steel status symbol (and the cost of that status symbol), why the Department of Transportation (DOT) is turning down special-permit requests, and why your freight rates are going up.

This afternoon I want to talk a bit about our new regulations and some of the interesting interpretations that have come out of their development.

Many things are disguised with misleading labels these days. You take a new airplane and load it down with G forces. You iron out the wrinkles and hand it over with all of its mechanical miracles in perfect working order—redundancy of backup systems, high-lift wing, and high-ratio bypass engines. And then they paint it purple, and the stockholders give Pucci all the credit for a beautiful work of art. Our new regulations are in themselves a work of art, but it would certainly be presumptuous to claim them as our own. Many of you put some very hard work into developing the new rules, into massaging them into their present form, and into getting the word around on their meaning. All we did was to publish them; yet, they will be ever known as the DOT's regulations. But we have only made a start.

Our progress since the first symposium in Albuquerque in 1965 has been truly phenomenal. The copy of the new rules,[2] which each of you found in your folders, represents the most far-reaching single regulatory effort in the field of hazardous-materials transportation and perhaps even in nuclear safety. I hope that each of you looks over the new rules before you leave and that you feel completely free to badger me in the halls or in my room to talk about them, because I too like to talk about them.

Changes

The new rules will wipe out all the existing Bureau of Explosives (B of E) permits as of Feb. 28, 1969. As of that date, all those packages must either meet the new standards or suffer the fate of a special-permit review. You should also know that the cutoff date for shipments in B of E permit containers into Canada is 2

*This paper was presented at the Second International Symposium on Packaging and Transportation of Radioactive Materials, Gatlinburg, Tenn., November 1968 in lieu of, and in addition to, the paper by the author which was included in the conference proceedings.[1]

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months earlier—Dec. 31, 1968. We expect a mass of special-permit applications early next year (1969) to cover these old rascals and have a few aces up our sleeves to take care of them. First of all, for Type A quantities, we don't plan to issue any deviations from the regulations. The new Specification 7A should cover all of them. For small lead casks for Type B quantities, we will have an interim wooden overcoat specification, along with a general special permit for its use. If your cask doesn't meet the new rules, put it in a wooden jacket. We can easily handle the few exceptions to that solution. Large quantities and fissile materials have already been pretty well covered by earlier cutoff dates by the AEC.

International Shipments

We have some more changes coming up in the future. We plan to incorporate more of the International Atomic Energy Agency (IAEA) general criteria throughout the regulations, and to reduce the differences between U. S. and international standards to a minimum. We will have a few more specification packages coming up—UF_6, the wooden overcoat, a birdcage for low enrichments, and a Type B cask. You should expect to see them within a year or so.

This is an international symposium, and so it is proper to talk about international shipments. Section 6 of the IAEA regulations covers the issuance of competent authority certificates. The DOT is the United States' competent authority, and the IAEA-type certificates are usually included in the DOT special permit. But before we can certify, as the competent authority, that your package meets IAEA criteria, *you* must first make that determination. And then you must tell us. All Type B, large quantity, and fissile shipments overseas must have an IAEA-type certificate from the DOT. And we can't issue it until you have assured us that you have checked the IAEA regulations and have satisfied yourself that your package meets the criteria. And then we want to see it from you in writing. We'll pretty much take your word for it, but we want you to realize where the responsibility lies for making the determination. You must give us your basis for determining that your capsule meets the special-form definition. You must look at the large quantity criteria in IAEA and tell us into which category your package falls.

Now there are a few differences between the IAEA rules and our own. One is the point of measurement for external radiation. Another involves an IAEA requirement for metal receptacles for liquids: we have not specified the material, but only the level of performance—"Thou shalt not leak!" We do not plan to issue IAEA certificates for Type A quantities of special form material; the other countries know that and won't expect to see one. We hope to iron out these differences with IAEA over the next couple of years so there will truly be complete harmony between the two sets of rules.

Special Permits

I want to spend a few minutes talking about justification for special permits. The regulations, Part 170, state that you must justify your request for a special permit. What does that mean? The rules provide for a number of specification packages, but there are a lot of holes. Where there is no specific package provided for, we will consider issuing a special permit for something different. But where one is provided, you must justify not using it. Convenience is *not* a justification. What is? We look at three things in an applicant's justification statement—safety, need, and public interest. At the risk of sounding callous, I can skip over the safety evaluation—the criteria are quite well known. They may be complicated, but if you're going to be in the ball game, you'd better plan to play on the first team or you'll never make it. Let's look at need. Does the person *need* the special permit, or will some other package do as well? Does he *need* his own special package, or do the regulations need changing? Many people think that special permits are a right, not a privilege. In some cases they are, but not always. We want to be responsive to public need and to economics, but cannot change the government's regulatory process merely for the convenience of an individual—which leads me to talk about public interest.

Public Interest

Before we can issue a permit, we must be assured that the request is in the public interest. What is that? Some people think that furtherance of atomic energy programs is sufficient public-interest justification for a special permit, or that providing a safe package is in the public interest. Now I would be the last to disagree with these lofty goals, but they don't necessarily justify DOT approval of a package. Public interest means that one of these three conditions is met:

1. To the general advantage of the public, rather than to the specific advantage of a single person or small group of persons.

2. Justifiable in terms of expenditure of public funds for the convenience of a single person or small group of persons.

3. Of a nature that would not be prejudicial to the interests of a large group of persons in favor of the interests of a single person or small group of persons, either in terms of unfair economic advantage of one person over another or in terms of undue risk of danger to the public.

Now, how does all of that fit here? In my published paper I discuss the cost to the taxpayer of issuing and administering a special permit. It runs anywhere from one to five thousand dollars. These are public funds. We issue a couple of hundred radioactive materials permits each year. This totals from 200 thousand to a million dollars. If we can cut that program by a hundred thousand, perhaps I can hire enough people to get your permits out in a timely manner. However, before we expend those public funds on a permit, we must be sure that the public interest is being served by the request. If some project manager wants his own private cask as a status symbol, that's not public interest. He should borrow or rent someone else's. If the rules allow six lump-lumps to be put in a box, and he wants to put in six and a half for better economics, that's not public interest. It's *his* interest, but not *public* interest. If he has 50 old birdcages that he doesn't want to modify to meet the new specs because it will cost him $5 a drum, that's not public interest. The government should not spend a few thousand of the taxpayer's money to save him $250. Maybe the regulations should be changed to be made more flexible; we'll welcome any concrete suggestions along that line.

License–Permit Relationship

Let me turn now to another subject. Many people think that because they get an AEC license under Part 71, they are automatically entitled to a DOT special permit. The AEC only looks at the criteria in Part 71—or *AEC Manual,* Chap. 0529. They don't necessarily heed some of the special transportation considerations. For example, we received some recent applications for Fissile Class III shipments. The AEC license allowed up to 2500 55-gal drums per truck. If you've ever tried to stuff that many drums in a truck, you'll know what a blivet is. Most truckers won't put more than 80 drums in a truck because if they double tier them, the top layer is likely to go right through the thin aluminum sides when he takes a corner too fast. But from a nuclear viewpoint, 2500 is an acceptable number. Don't expect the DOT to authorize more than 80. And you shouldn't expect us to authorize Fissile Class III shipments by air without a searching examination. Of course, if you really plan to have exclusive use of the Boeing 707, or plan to accompany it as an escort—in a separate plane, of course—we'll be happy to accommodate you. If you want to ship by air, better plan on Fissile Class II, which leads to another problem.

The Fissile Class III provisions are meant to be used only in the event that you can't meet the requirements of a Fissile Class I or II shipment. Many people want to use Fissile Class III merely as a dodge to avoid a calculation. Obviously, a spent fuel cask weighing 50 tons, containing a kilogram of ^{235}U plus a megacurie of fission products, can probably go as Fissile Class I, or certainly as Class II. But you have only one cask anyway; so why bother with the calculation? Everybody knows that it can't go critical, so call it Class III and forget it. We're entering into a new phase in living with the revised rules, and we ought to develop good habits now before they become so ingrained that we lose sight of the purpose of the flexibility.

Containers

New subject, old topic: saving money on birdcages. You know, some of the lighter gage drums were designed for only a few trips. Rough handling is common, and the drums take a real beating, e.g., corrosion and damaged chimes and lips. Repainting is often necessary. Some people have found that they save money in the long run by making their drum-type birdcages (6M, 6L) out of stainless steel. The initial cost is higher, but the maintenance is so much lower and the life so much longer that they save money. This is particularly true if you ship less than trailer load quantities via commercial common carrier.

Padlocks: probably half of the spillages of radioactive materials in transportation involve the use of a padlock as a closure device. Many of them are screwed into the lead itself. People wonder why they aren't acceptable! Our rules require a positive closure device. We consider that a bolted flange, or a locking-type plug, would meet that requirement but not a padlock. There might be some exceptions, but as a general rule they don't make it. The closure device must not be able to be knocked off during the normal type of rough handling of these packages. Padlocks can easily get knocked off, and experience proves it. A padlock

isn't even sufficient to meet the requirements for a security seal because you can't tell whether it has been illicitly opened.

Enforcement

Many of you think there is no enforcement of the DOT regulations. Perhaps we just haven't given enough publicity to our enforcement actions. We had three enforcement actions last week, and here are the results: (1) a trucker who left his truckload of explosives unattended at a restaurant was fined $1000; (2) a shipper was fined $1500 for not using specification containers and for filling out his shipping papers improperly; (3) another shipper—represented here, I'm sure—was fined $300 for improper labels and failure to properly certify his shipping papers. Of course, the fines are a small part of their costs—it takes thousands to defend a federal criminal suit.

We've made a lot of changes—and I say "we" as an industry—and now we must live by them. We'll be patient with you, and we hope that you'll be patient with us. Naturally, dramatic change can produce uncertainty, disorder, and even resentment. Some people cry and caterwaul for the good old days. They demand that the world be stopped so they can get off. I plan to ride for a while, and I hope that most of you do, too. (REG)

References

1. *Proceedings of the Second International Symposium on Packaging and Transportation of Radioactive Materials*, Oct. 14–18, 1968, Gatlinburg, Tenn., USAEC Report CONF-681001, 1968.
2. Part II, Department of Transportation, Hazardous Materials Regulations Board, Radioactive Materials and Other Miscellaneous Amendments, *Federal Register*, 33 (194): (Friday, Oct. 4, 1968).

Ion-Exchange-Resin System Failures in Processing Actinides*

By F. W. Miles†

[In January 1967 an ion-exchange resin column exploded at ORNL while being used to separate curium and americium in a $LiNO_3$ solution. The editors of *Nuclear Safety* felt that similar events, particularly in bench-scale tests, might be prevented at other installations if an appropriate set of recommendations were developed. It was discovered that six other occurrences had been reported in recent years involving various types of failures (fires, ruptures, explosions) in resin-exchange systems that were being used in nuclear work. The following article was commissioned from ORNL's Chemical Technology Division to investigate the reported events, study the results of five subsequent studies, and present a unified report together with appropriate recommendations and guidelines. The five studies discussed general effects and were directed primarily at certain continuous processes; there generally exists no extensive verified set of data that is particularly pertinent to the small-scale chemical investigator.—E. N. Cramer, Sec. VI Editor].

Abstract: Seven instances of ion-exchange-resin system failures have been reported in nuclear work since June 26, 1962, and five studies have been made of the thermal stability of nitrate-form resins. All instances apparently involved the self-ignition of nitrate-form resins (with both aromatic and aliphatic matrices) in strong (>7N) nitric acid in the presence of some amount of heat. In one of the studies, a chemical mechanism was postulated whereby an uncontrollable reaction can occur with the nitrate-form anion resin in strong HNO_3 solutions. Two groups of precautionary measures are suggested: (1) those associated with the chemistry of resins, such as maximum operating temperature and ionic loading limits, and (2) those common to chemical processing, such as pressure-relief devices and adequate rules concerning procedural changes.

The published accounts and related articles dealing with untoward occurrences that have taken place in recent years in nuclear work with anion-exchange resins are reviewed in this article and discussed as a unified whole. The cause or causes of accidents are set forth, and safety guidelines are proposed to minimize the number and/or effects of such accidents in the future.

The anion-exchange resins of interest in this study are primarily of the strongly basic type and are frequently used in nuclear work. Dowex 1 (Dow Chemical Co.) and Amberlite IRA-400 (Rohm and Haas Co.), for example, are polystyrene–divinyl benzene polymers, with the active group being a quaternary ammonium group. Such resins are normally received

*This article is reproduced with the kind permission of the Editors from *Nuclear Safety*, 9(5): 394-406 (Sept.–Oct. 1968), since it is believed that it will be of interest to readers of *Isotopes and Radiation Technology*.

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from the manufacturer in the chloride form and converted to the nitrate form by the user.[1] In at least two cases, however, the nitrate form of the resin was supplied by a distributor.[2,3]

The resin column is typically a cylindrical vessel of glass or stainless steel. As used in fuel reprocessing, it is probably 1 to 10 in. in diameter and may range from 1 to about 10 ft in height. The resin is placed within the column and is held in place by suitable retainers at the bottom and top. The resin bed in most resin columns is stationary. At Hanford, however, the bed moves through the column (contactor) on a programmed cycle.

The solution containing the actinide complex ion to be extracted is pumped in an axial direction through the column at a specified temperature and flow rate. As the solution flows through the column, the actinide complex ion sorbs on the resin and is later removed from the resin by "elution," when a suitable solution such as 0.35*N* HNO_3 (termed "eluant") removes the metallic ion from the resin as it is passed through the column. The directions of flow during absorption and elution are not always the same but depend on the system.

When actinides are being processed, the ion-exchange column and associated equipment are generally contained within a glove box or a closed cell to provide protection against the release of radioactive species to the surroundings. When radiation shielding must be provided to protect personnel from penetrating radiation, the equipment is operated remotely.

Two of the many works published about ion-exchange resins are one[4] that describes the general field, and one[5] that particularly describes plutonium processing.

Accounts of Resin System Failures

Seven occurrences have been reported during the past few years in nuclear work with anion-exchange resins which resulted in system failures. Six occurrences took place with aromatic-matrix resins that were used in the separation of actinides such as plutonium, curium, and uranium from other elements. One failure, an explosion, occurred in the heavy-water purification system of a nuclear reactor in which the system contained an aliphatic-matrix resin. A detailed account of each incident is given below.

*FONTENAY-AUX-ROSES, JUNE 26, 1962 (OCCURRENCE 1)**

A glass anion-exchange column, used in the purification of plutonium solutions, ruptured in a glove box in the radiochemical building at Fontenay-aux-Roses, France.[6] Small batches (approximately 10 g) of plutonium in nitric acid solutions were normally purified by a sorption–elution cycle at 25°C with Dowex 1-X4 anion-exchange resin in a pyrex-glass column 20 mm in diameter and 250 mm long and filled to a height of 150 mm. The resin in use at the time of the rupture had been used several times previously in purifying plutonium. In the procedure, 350 ml of a nitric acid solution (10*N* to 12*N*), containing 50 g of plutonium per liter was passed through the resin column to saturate the resin completely with the plutonium nitrate complex.

Scrubbing the impurities from the resin column with 7*N* HNO_3 is required prior to eluting the plutonium; this was not done until 4 days after the plutonium was loaded on the resin. At that time the resin column was filled with small bubbles, and the color of the resin was a dark brown that possibly indicated nitration. As soon as the operator started the scrubbing operation, the glass resin column ruptured with sufficient violence to disperse the column and its contents throughout the glove box and to cause several cuts on the hands of the operator.

The conclusion in the final report[6] was that the force that caused the rupture resulted primarily from prolonged exposure of the anion-exchange resin to high concentrations (10*N* to 12*N*) of HNO_3. Recommendations made were that (1) the acidity of the HNO_3 solutions used in plutonium purification be limited to 7.5*N*, (2) the acidity determination be made before each operation, (3) the resin–acid contact time not exceed 24 hr, and (4) the temperature of the anion-exchange contactor not exceed 30°C. In addition, limiting the particle size of the resin used in plutonium purification to 50 to 100 mesh was suggested to reduce the tendency of the resin to form plugs that might result in high pressure drop and poor cooling within the column.

ROCKY FLATS, JULY 14, 1963 (OCCURRENCE 2)

Plutonium was recovered at Rocky Flats from the peroxide filtrate stream by ion exchange.[2,7] Each nitrate solution was concentrated to 7*N* to 8*N* HNO_3 and 40 g of plutonium per liter by evaporation and then was fed to three series-connected contactors. Each contactor was constructed of 6-in.-OD pyrex-glass pipe, 30 in. long, with stainless-steel top and bottom fittings. The columns were loaded with 50- to 80-mesh Dowex 1-X4 anion-exchange resin.

Four hours before it gave way, the first column had been loaded with 8*N* HNO_3 containing 40 g of plutonium per liter at ambient temperature (25 to 30°C) and isolated from its feed line and the other two columns by closed valves. Apparently a reaction between nitric acid and either the loaded resin or some extraneous organic material, such as hose plasticizer, generated reaction products in the column

*Numbers are assigned to these events to facilitate later discussion; the numbers do not correspond to the chronological sequence of the events.

until the pressure was high enough to rupture a gasket. The hot partially oxidized resin that was expelled started a fire that burned the gloves in the glove box and spread contamination. The fire was extinguished within 90 min by using CO_2 and MgO sand. Microscopic examination showed that most of the resin beads had been blackened and were fused rather than fractured.

Although a temperature of at least 500°C was required to convert a green plutonium-loaded bead to the black fused form,[7] other laboratory tests of production-scale (4-in.-diameter) vented ion-exchange columns have indicated that the critical ignition temperature for plutonium-loaded resin would be well below 100°C (Ref. 1, p. 29).

The evaluating committee suggested venting procedures for temporary shutdowns and pressure-relief devices. They also recommended studies relative to the magnitude and causes of gas evolution from plutonium-loaded anion-exchange resins and devices and studies of the compatibility of nitric acid with plutonium-loaded resin.[7]

HANFORD, NOV. 6, 1963 (OCCURRENCE 3)

Plutonium was purified in the Redox plant at Hanford by the ion-exchange technique.[8,9] The contactor used for this purpose was a loop of 4-in. pipe divided into sections with motorized valves operated by a cycle timer at a temperature between 85 and 90°C. Plutonium, as the anionic complex, was removed from the solution onto the resin in the extraction section of the contactor. Impurities were removed from the plutonium-loaded resin by a 7*N* HNO_3 stream in the scrub section. Purified plutonium was eluted from the stripping section with dilute HNO_3 ($\leq 1N$).

Early on the day shift of Nov. 5, 1963, the nitric acid scrub-recycle line became plugged. This line normally supplied about 75% of the total acid feed to a concentrator to make it possible to produce 7*N* HNO_3 from the concentrator without adding makeup acid to the system. A temporary piping connection was made to permit periodic adjustment of the nitric acid concentration of the plutonium nitrate solution in the feed tank to the concentrator. This temporary piping arrangement involved a direct tie-in to an existing system of two tanks with interconnected piping; one tank contained nitric acid, and the other, a solution of sodium dichromate. Because the nitric acid additions were not made on a regular basis, plutonium losses in the contactor waste stream were higher than normal. Although proper adjustment of the nitric acid concentration in the feed tank was made during the next working shift, plutonium losses were 10 times normal, and 90% of this plutonium was in the +6 valence state.

At approximately 1:23 a.m., November 6, a sudden reversal of air flow was noted in the building, along with a detectable vibration of the instrument panel board as air from the process area was forced into the operating gallery. The operation of the facility was immediately shut down remotely. About 30 min after the first event, radiation monitoring personnel investigating the incident found that a fire had broken out. Because of the criticality hazard, the fire was extinguished with dry chemical extinguishers (sodium bicarbonate). The Redox plant was shut down for approximately 6 weeks as a result of the fire damage to the building and equipment, the alpha contamination and associated cleanup, and normal maintenance. No injuries, radiation or otherwise, resulted from the occurrence.

The inadvertent addition of sodium dichromate solution, a vigorous oxidant, to the system during the afternoon or evening of November 5 was apparently the origin of the incident. The dichromate solution gradually worked through the system and into the anion-exchange contactor, where it initiated degradation of the resin and probably participated in an exothermic reaction that heated a portion of the resin to well above the 85°C operating temperature. The entire load–scrub section of the contactor was pressurized to more than 1500 psi by evolution of gaseous products. This high pressure caused expansion of the schedule-10 piping in that section, followed by gasket rupture and the spraying of a high-velocity stream of resin and acid from between the flange faces. The resin–acid stream ruptured containment barriers on three sides of the contactor, sprayed material to distances of 8 to 10 ft away, and caused an air flow reversal that was noted by the operators in the operating gallery, as mentioned above. Hot gases and/or resin beads from the contactor started a fire that burned at low intensity.

This incident initiated the studies by Fullam[1] and by Van Slyke, Jansen, and Swift.[10] Recommendations made following the investigation included:[8]

1. Providing adequate pressure relief.
2. Incorporating hydraulic and mechanical design features in the exchange contactor to minimize the risk of forming stagnant gas pockets in the resin.
3. Establishing controls to evaluate resin quality and thereby assure that the resin does not have excessive loading capacity.
4. Establishing procedures that will assure control of nitric acid concentration at a minimum practical level (7.8*N* to 8*N* maximum) and that will preclude inadvertent addition of oxidizing chemicals to the system.

ORNL, JANUARY 1967 (OCCURRENCE 4)

An anion-exchange resin column was used at ORNL in the purification of ^{244}Cm (Ref. 11). The lithium nitrate solution being processed contained 8 g of curium, about 1 g of ^{243}Am, and about 5 g of calcium. The purification was based on the sorption of curium and americium on the Dowex 1-X10 resin bed while

the calcium passed through. The curium and americium were separated by selective elution.

The glass column, 2 in. in diameter and 24 in. high, contained resin to a height of about 18 in. which was held down by glass wool and glass beads. The column and associated equipment were located in a hot cell.

Prior to being fed to the column, the lithium nitrate solution had been concentrated by evaporation and allowed to cool overnight. Dark-brown nitrogen oxide fumes occupied the void space above the solution. The $LiNO_3$ concentration of the solution was about 8*N*, and the HNO_3 concentration was less than 0.1*N*. As the solution was fed onto the column, a dark-brown area appeared on the top of the column. Near the end of the feed period, the generation of brown nitrogen oxide fumes in the column was apparent. When all the solution had been fed, the column was vented, and preparations were made to strip the curium off the resin with 0.5*N* HNO_3. The column vent was closed, and the 0.5*N* HNO_3 was fed to the top of the column. Before the dilute acid had reached the curium band, however, the column exploded.

The column was completely destroyed, with the largest piece being no more than 1 sq in. in area, and the resin was uniformly spread over all surfaces of the cell. The integrity of the cell liner was verified when a radiation survey revealed that no activity had leaked from the cell. Other than a curium loss of about 5% and the loss of some equipment and recovery time, no serious consequences resulted from the explosion.

The explosive pressure buildup was believed to have been caused by heat from the relatively large amount of curium accelerating the nitration of the resin and raising the temperature to a point where an exothermic reaction occurred. Since the heat input from the ^{244}Cm was about 20 watts in a resin volume of 25 to 50 cm^3, the temperature of the nominally 80°C column could have exceeded 125°C in the section loaded with curium.

Recommendations for future laboratory-scale work with this system were[11] (1) to limit the amount of ^{244}Cm to 1 to 2 g and (2) to perform the work at room temperature.

KERR-McGEE, MAY 24, 1967
(OCCURRENCE 5)

A rapid chemical reaction occurred at the Kerr-McGee Cimarron Facility in an ion-exchange column during resin regeneration.[12] An insignificant quantity of source material, collected as depleted uranium from process waste streams on the IRA-400 anion resin, was being stripped from the resin column with nitric acid. A pressure buildup ruptured the ion-exchange column and scattered pieces of the metal vessel and acid-laden resin. No personnel injuries resulted. Health-physics surveys verified that no significant release of radioactive material occurred.

Ad hoc review of the occurrence did not achieve a completely clear-cut definition of the causes. The most probable explanations of the column failure were considered to be the following. The equipment for blending concentrated nitric acid and water malfunctioned in a manner to permit a "plug" of nitric acid solution more concentrated than that planned to be fed to the column. The plug of nitric acid was heated by dilution with water, by the exothermic reactions of dissolution of solids filtered out of the resin bed, and by the reaction whereby sorbed uranium was eluted from the resin. Through this sequential heating the concentrated nitric acid plug reached a temperature sufficient to achieve an autocatalytic reaction with the resin bed which led to pressurization and ultimate rupture of the column.

The corrective actions taken to prevent recurrence included:

1. Batch makeup of the dilute nitric acid solution to avoid higher concentrations than desired and allow dissipation of heat of dilution.
2. Providing a rupture-disk pressure-relief system to the ion-exchange columns.
3. Regenerating with a continuous flow of nitric acid to allow partial dissipation of the heats of reaction outside the resin column.
4. Temperature monitoring of the effluent acid solution and procedural controls to preclude an excessive temperature increase in the resin bed.

BNL, JULY 23, 1965
(OCCURRENCE 6)

An anion-exchange bed was part of a water-treatment system for the Brookhaven High Flux Beam Reactor.[3,13] The bed was used to adjust the acidity of the heavy-water stream of the reactor; it was not used in the processing of actinides or any radioactive species.

The anion-exchange vessel was an assembly of stainless steel and lead with an internal volume of 7 cu ft filled with nuclear-grade Duolite A-30B (a weak base anion-exchange resin) that was supplied by the vendor (Diamond Alkali Co.) in the nitrate form. The vessel had been left filled with resin for several months at atmospheric pressure following a hydrostatic pressure test. In the meantime laboratory tests indicated that the resin failed to meet the required effluent chloride specification. Correspondence with the vendor culminated in the suggestion that the user renitrate the resin with 2*N* HNO_3. Laboratory-scale tests indicated that this procedure was satisfactory.

The 2*N* HNO_3 required for renitrating the 7-cu ft batch was prepared by emptying twelve 7-lb bottles of reagent-grade 70% HNO_3 into a drum, adding demineralized water, and stirring for a short time. This solution of nitric acid was then pressure transferred, using nitrogen from a standard cylinder, to the bottom of the anion-exchange vessel at a flow

rate of 0.4 gal/min. Since water immediately issued forth from the outlet lines of the vessel, it was concluded that the voids in the vessel had been initially filled with water. An explosion occurred about 10 to 20 min after the operation had begun. The developed pressure was probably between 1200 and 2500 psi. The operator, who was standing at floor level near the top of the vessel, was blown from his feet by the force of the explosion. Prompt action by other workers in the immediate vicinity probably minimized the extent of his injuries (burn-type lesions about his face and hands from the nitric acid and resin sprayed from the pit). Safety glasses saved his vision. The pressure transfer of the diluted HNO_3 was believed to have had no effect on the explosion, although it is not recommended as a safe means of transfer. A later analysis of the nitrogen gas in the cylinder appeared normal, and the regulating valve on the cylinder was found to be in good condition.

The explosion was undoubtedly caused by pressure buildups resulting from the HNO_3/resin reaction. Two factors that either alone or together were capable of initiating the explosion were incomplete mixing of the nitric acid solution prior to adding it to the vessel, with the result that there were high local concentrations, and a temperature rise in the acid solution associated with the heat of dilution of HNO_3 in water. Factors that may have contributed to the trouble were the effect of the large-scale nitration of an aliphatic-based anion-exchange resin and the effect of catalyzing ions, such as iron and chromium, which may have been leached by the water from the vessel during the long standing period.

On the basis of the experimental work and the violent explosion that occurred when the resin was re-treated with HNO_3, two distinct possibilities emerged[3] as being responsible for the accident: the accumulation of a concentration of nitrate esters resulting from previous HNO_3 treatment by the vendor that, when augmented by further nitration in situ at BNL, yielded a thermally unstable polynitrate, and esterification of the alcohol functions and attendant formation of HNO_2 via oxidation of the alcohol by the relatively concentrated HNO_3.

Certain precautionary measures should therefore be taken in similar operations: the nitric acid solution should be determined to be of the proper concentration before use in resin nitration, and the resin should not be allowed to stand for a long period of time before use because of changes that may occur, such as drying of the resin or leaching of catalyzing ions from the container.

SAVANNAH RIVER, OCT. 1, 1964
(OCCURRENCE 7)

An anion-exchange column was used at the Savannah River Plant to recover neptunium from Purex high-activity waste.[14] The entire recovery facility was located in a hot canyon, and all operations were performed remotely.

Remote repair work was in progress to remove a plug in the piping of the anion-exchange column. The column had been emptied of resin, and flushing of the column and associated piping with water and 60% HNO_3 had been under way for several shifts. During this work various spilled materials, including high-activity waste concentrate and degraded nitrated resin, had accumulated around the column. A small leak (~0.5 gal) of 60% HNO_3 occurred in the line that supplied chemical feed to the column; the spilled HNO_3 apparently reacted with the accumulated solids, and the heat of reaction, combined with self-heating from the high concentration of fission products, resulted in spontaneous ignition and fire. The fire was extinguished by the hot-canyon water-spray system.

As a result of the fire, airborne contamination collected on the hot-canyon crane, and water damaged the electric motors on the agitators for the anion-exchange column and the column feed tank. The total damage to equipment plus the cost of decontaminating the crane were estimated to be $21,000.

The true cause of the fire was not definitely established because of the inaccessibility of the location in which it occurred. It was known, however, that the nitrate form of the anion-exchange resin was flammable when dry. It was also known that the fire did not occur in the column (since all the resin had been removed and the column was filled with 60% HNO_3) and that the temperature of the column did not exceed 35°C either before or during the fire.

The recommendation was that a spray system for flushing the external surfaces of such a column might prevent the recurrence of a similar incident. Sodium hydroxide solutions (concentrations unspecified) were considered to be desirable flushing media.[14]

Thermal-Stability Studies of Resins

Available information on thermal-stability studies of nitrate-form anion-exchange resins in nitric acid is discussed below. These studies were initiated by the occurrences discussed above.

HANFORD STUDY

Fullam[1] examined Dowex 1, IRA-401, and Permutit SK (Permutit Co.) in an open system. He found that, when a nitrate-form anion-exchange resin was heated above a certain critical temperature (termed "self-ignition temperature") in an open system, a thermal excursion resulted. Most of his work was done on a small scale with a resin volume of less than 10 ml; however, some unloaded resin work was carried out with volumes up to 1000 ml.

His experimental results showed that the absolute value of the self-ignition temperature for anion

resins on a small scale depended on a number of factors:

1. Resin form — With unloaded anion resins, only the nitrate form exhibited self-ignition. The chloride, sulfate, and hydroxide forms simply charred on heating.

2. Heating rate — More rapid heating led to a lower ignition temperature.

3. Resin brand — Thermal stability varied greatly from brand to brand.

4. Cross-linkage — Increased cross-linkage gave a lower ignition temperature.

5. Loading — When an anion resin was loaded with a nitrate-containing complex [i.e., $Pu(NO_3)_6^{2-}$, $Th(NO_3)_6^{2-}$], the ignition temperature decreased as the loading level increased.

6. Resin volume — Increasing the significant geometrical dimension of the vessel lowered the ignition temperature.

7. Aging — Used resin exhibited a higher ignition temperature than fresh resin.

8. Pretreatment — The treatment given the resin prior to measuring the ignition temperature affected the result obtained. For example, if the resin was washed with nitric acid prior to testing, the ignition temperature depended on the normality of the acid used. The ignition temperature varied inversely with the acid normality.

9. An unknown factor — Although the temperature determinations were performed under carefully controlled conditions, the spread of the data was great enough to indicate the presence of at least one unknown factor.

The lowest ignition temperature determined was 135°C, which occurred with resin heavily loaded with plutonium. The volume of resin used in this test was about 1 cm^3. Larger volumes of plutonium-loaded resins (which were not tested) would undoubtedly give lower surface ignition temperatures because ignition would be initiated by a higher internal temperature resulting from heat generation within the volume of resin.

PACIFIC NORTHWEST LABORATORY STUDIES

Van Slyke, Jansen, and Swift[10] made a study on an engineering scale (4-in.-diameter by 6-ft-long column) in a closed system operating with Permutit SK in 7*N* HNO_3. The reaction kinetics for the system were investigated by externally heated pipe pressurization tests and by calorimeter experiments. The chemical and physical properties of the system were correlated by mathematical models for batch and flow cases with computer programs (FORTRAN II and IV) to predict the conditions that permitted self-accelerating chemical reactions. Uncontrolled reaction conditions were favored by

1. Increasing vessel radius.
2. Low heat-transfer coefficients from the vessel wall to the surroundings.
3. Low thermal conductivity of the vessel contents.
4. High ambient and operating temperatures.
5. Chromium(VI) loaded on the resin.

The theory, based on the concepts originally proposed by Frank-Kamenetskii,[15] is generally applicable to slabs, cylindrical shapes, and spheres that generate heat with an exponential dependence on temperature.

Occurrence 3 was discussed briefly in terms of this analysis and of Van Slyke's dynamic tests.[10] The high internal pressures created in the contactor undoubtedly resulted from a runaway exothermic gas-producing reaction caused by either an external heat source or an abnormal exothermic chemical reaction in the resin bed. Most of the evidence indicated that the contactor pressurization preceded the fire and that an internal reaction initiated the pressurization. This reasoning is supported by the presence of dichromate ion in the contactor feed. The spot chromium concentration reached at least 0.33 g/cm^3, and it was calculated that pressurization could occur at a holdup time of about 5 min at the recorded 87°C feed inlet temperature, based on the experimental data obtained in the study. Holdup times prior to the incident were about 22 min in the contactor scrub section and about 11 min in the feed (extraction) section. The presence of plutonium probably lowered the critical operating temperature — a factor investigated by Fullam.[1]

In a subsequent study, Van Slyke[16] investigated the reaction kinetics of five anion resins and one cation resin with 7*N* HNO_3; the tested resins were not identified in the report. The kinetics of a batch of one anion resin were measured at lower acid concentrations. Although the cation resin reaction kinetics were measured in 7*N* HNO_3 calorimetrically, the resin was too reactive to be equilibrated with 7*N* HNO_3 by the pipe pressurization tests.

Van Slyke[16] also investigated an anion-exchange process cycle used for ^{99}Tc recovery to find any dangerous circumstances. The steps in the anion-exchange process cycle were (1) alkaline feed, (2) alkaline wash (1*N* NaOH), (3) water wash, (4) nitration of resin (0.25*N* HNO_3), (5) elution (6*N* HNO_3), and (6) water rinse. All but one of the five anion resins were found to be reasonably safe for the process cycle, as calculated from their measured reaction kinetics and the ion-exchange system geometry.

Hazardous situations could occur under certain conditions: (1) if hydroxyl-form resin were converted to the nitrate form with too-strong nitric acid (>0.75*N*) instead of the intended 0.25*N* HNO_3, (2) if resin in strong nitric acid were allowed to stagnate in large-diameter vessels, and (3) if ion-exchange vessels containing organic resin in strong nitric acid

were operated with high radioactive heating rates (over 100 watts/cu ft) and for long liquid residence times (over 2 hr).

Dry resin that was burning could be quenched with water, although it was very difficult to get the resin dry enough to burn; it was also found that dry resin was not shock-sensitive to a No. 8 blasting cap. A film was prepared containing four sequences of the calculated time–temperature behavior of the exothermic reactions obtained.[17]

Recommendations[16] were that (1) precautions should be taken to prohibit unusual operating conditions that could cause severe exothermic effects, (2) thorough temperature instrumentation should be used to detect a developing hot spot in the ion-exchange vessel in time to prevent a chemical excursion, (3) temperatures should be watched very closely when nitric acid is flowing, (4) the best known remedy for excessively rising temperatures discovered during operation is a reverse flow of cold water through the ion-exchange vessel, and (5) pressure relief should be incorporated into the ion-exchange facility.

ROCKY FLATS STUDY

Molen[18,19] performed a two-part study to analyze Occurrence 2, which took place at Rocky Flats. In Part I of the study,[18] Molen summarized his work as follows:

> Dowex 1X4 nitrate form resin was treated with nitric acid at varying temperatures and for varying time periods. Mayon, Tygon, and thermoplastic tubing were similarly treated. The treated resin, and extracts from the treated resin and tubing, were found to react exothermally at temperatures as low as 135°C. The smoke which evolved from these reactions would burn and, on occasion, explode when ignited by a spark gun.
>
> Forming ClF_3 by reacting chloride leached from tubing with fluoride in the feed stream to a column was considered to be highly improbable.
>
> Analysis of gases formed when resin was contacted with nitric acid in a pressure vessel indicated a C–C bond cleavage. This postulate was based on the excess of CO_2 found in the gas mixture.
>
> Extraction of resin with nitric acid gave inconsistent results. The amount of insolubles found in the extract did not always increase with time and increased acid concentration. The extract was insoluble in carbon tetrachloride and soluble in water. Attempts to identify the extract by infrared analysis were not successful. Concentrations of approximately 7*N* HNO_3 or greater were required to produce significant quantities of resin extract.
>
> Reactions of NO_2 and N_2O with various glovebox materials produced nothing that would ignite spontaneously.
>
> Others at Rocky Flats found the following:
>
> 1. Phthalic anhydride, *o*-phthalic acid, dioctylphthalate, and butylphthalylbutylglycolate were present in the tubing extracts.
> 2. Chloride could be leached from the tubing. The least amount was leached from Tygon tubing.
> 3. Although pressure buildup did occur in an ion column when not vented, no significant temperature rise was measured.

Using Dowex 1-X4 and 7*N* HNO_3 in a closed system without radioactivity, Molen[2,19] found in Part II of the study that the resin pyrolytically decomposed at less than 200°C when the liquid content was less than 50%. The magnitudes of the ignition temperature and pressure varied directly with the liquid content of the resin, whereas the maximum temperature and pressure at the time of the gasket rupture varied inversely with the liquid content of the resin, as shown in Table 1.

Table 1 .TEMPERATURE AND PRESSURE CONDITIONS AS A FUNCTION OF LIQUID CONTENT IN RESIN

Liquid content of resin, %	Conditions at ignition		Maximum conditions at rupture	
	Temp., °C	Pressure, psig	Temp., °C	Pressure, psig
40	165–180	150–350	200–500	250–1000
20	125–200	30–130	350–1000	300–>5000
5	<200	Unreported	1000	>10,000

The mechanisms of the ignition and rupture were postulated in two steps. First, the nitrite ion, which may occur in nitric acid as a manufacturing impurity or as a decomposition product, reacted exothermically with the quaternary ammonium sites (nucleophilic attack) on the resin to produce gaseous trimethyl amine and methyl nitrate. An intermediate electrophile resulting from electrophilic displacement was probably formed. When the temperature and pressure of the gaseous mixture reached the proper values, ignition occurred with accompanying high temperature and pressure. Because the decomposition of the resin occurred in the millisecond time range, rapid-response instrumentation was essential.

Similar results were postulated for the Permutit resin. However, since the Permutit resin apparently contains pyridinium sites instead of quaternary ammonium sites, the organic species formed by the action of the nitrite ion on the sites were postulated as nitrogen containing alcohols and organic acids. Ignition and the accompanying high temperature and pressure were nevertheless observed; but, in general, the Permutit resin was somewhat less reactive than the Dow resin.

Recommendations were:

1. To provide a column vent and install a rupture disk for ion-exchange operations with HNO_3 concentrations of 2*N* and greater.
2. To add a small concentration of sulfamic acid to the nitric acid solution to react with the nitrite ion.[20] At Rocky Flats, 7.5*N* HNO_3 is made 0.1*N* in sulfamic acid.

BNL STUDY

A study[3] was made at Brookhaven National Laboratory in an effort to determine the cause of Occurrence 6. The resin studied was nuclear-grade Duolite

A-30B (also termed Duolite ARA-368), which is a weakly basic anion resin. It is a matrix of polyethylenediamine cured with epichlorohydrin, and it contains tertiary amine and quaternary ammonium exchange sites, as well as apparently secondary amine groups. Reactive groups present in the resin are tertiary (aliphatic) amines, secondary (aliphatic) amines, secondary alcohols, quaternary ammonium nitrogen, unreacted epoxy groups, and aliphatic chloride. The direct applicability of the results of the other studies to the BNL situation is questionable because an aromatic matrix was considered in the other studies.

The study consisted in heating resin in the presence of 2*N* HNO_3 at temperatures between 60 and 85°C and making predictions of unstable compounds that might have been formed in Occurrence 6. The laboratory experiments demonstrated that extensive chemical reactions can occur between the resin and HNO_3 and that the resin becomes more susceptible to reaction upon prolonged standing in water or concentrated HNO_3, as operating experience has indicated, with the additional possibility that repeated recycling with dilute HNO_3 might have a similar "sensitizing" effect. The postulated unstable compounds included an aliphatic derivative of ammonium nitrate and esters formed from alcohol groups and nitric acid.

In the esterification of alcohols by HNO_3, the presence of considerable amounts of HNO_2, which may be formed as a reaction product, can lead to explosive decomposition. The usual practice is to add small quantities of urea during such esterification to destroy HNO_2 as it is formed, and the temperature of the reaction mixture is usually maintained between 0 and 10°C to avoid oxidation of the alcohol and attendant formation of HNO_2 (Ref. 21).

The BNL study[3] developed several long-range recommendations, of which two are particularly pertinent:

> 1. Except on a laboratory scale, the treatment or regeneration of aliphatic based ion-exchange resins with nitric acid should not be carried out until further research establishes the conditions under which such an operation can be safely performed.
>
> 2. A research program should be instituted to study the observed instability of commercially available anion exchange resins in contact with nitric acid (and other oxidizing agents). This study should begin with the extensive and valuable data already compiled by the investigators at Hanford, and other reported data, and cover the various operational parameters involved in any of the processes using this system that are of interest to the AEC.

Evaluation of the Occurrences Based on the Factors Mentioned in the Studies

The factors affecting resin stability given in the five studies are listed in Table 2, along with notations of their presence or absence in each of the occurrences. Four factors were present in all the occurrences: (1) resin in the nitrate form, (2) high concentration ($\geq 7N$) of HNO_3 or nitrate ion, (3) some source of heat, and (4) low thermal conductivity of the resin. In three cases (Occurrences 1, 2, and 7), heat from the reaction between nitric acid and the resin was assumed to be the source of heat. In the other occurrences several sources of heat were present in addition to that derived from the reaction of the resin with nitric acid. These included heat from radioactive decay and heat of dilution of nitric acid with water, as well as operation of the column at higher than ambient temperature. Poor dissipation of heat from the resin beds, as mentioned by Van Slyke, Jansen, and Swift, would also be a contributing factor. Resin beds would have poor heat-removal characteristics because of the low thermal conductivity of the resins [about 0.25 Btu/(hr)(sq ft)(°F/ft)]* and the static nature of the resin beds. Extraneous materials were probably present in about half the occurrences. Note also from Table 2 that in six of the incidents the resin bed stood for more than 1 hr; this allowed considerable contact time between the resin and strong nitric acid. Apparently during these long contact times the beds were heated to the self-ignition point by the various sources of heat. In addition, pressure buildup would occur if the system was closed. The effect of a closed system was not clear-cut since two of the systems involved were vented. The effect of the solution content of the resin could not be determined because of lack of data.

Two of the factors postulated in the studies (freshness of resin and rate of heating) were generally not reported and were therefore omitted from Table 2. If the quaternary ammonium sites are the sources of attack as postulated by Molen,[19] fresh resin would be more reactive than used resin because it would contain more sites.

The drying out of resin seemed to be a factor in only one occurrence. However, the importance of this factor should not be minimized, as discussed below under the heading "Precautionary Measures Associated with Using Resins."

The explosion that took place in the heavy-water purification system of a nuclear reactor, prior to the introduction of radioactive material, indicates that such occurrences are not limited to the processing of actinides. Some evidence also exists for the occurrence of two incidents with ion-exchange resins elsewhere, one in nonnuclear (pharmaceutical) work, and the other in uranium processing in South Africa.

*Calculated by taking the average thermal conductivity of resin in a column having water in the voids between resin particles. The resin was assumed to contain 50% water, and the void fraction was taken as 0.50. This value agrees with the reported value of 0.24 Btu/(hr)(sq ft)(°F/ft) for a 20- to 50-mesh resin.[16]

Table 2 FACTORS FOUND TO BE IMPORTANT IN STABILITY STUDIES OF ANION-EXCHANGE RESINS

	Activity present and Occurrence No.*						
	Moderate actinide concentration in solution				Low actinide concentration in solution	No radio-activity	Actinide present (amount unspecified)
Factor	1	2	3	4	5	6	7
High concentration HNO_3 ($\geq 7N$)	X	X	X	X†	X	X†	X‡
Above ambient temperature	0	0	X	0	?	0	X
Source of heat							
Radioactive decay heat	?	?	?	X	?	0	X
Heat of dilution of acid in water	0	0	0	X	0	X	0
High heat of reaction	0	0	X	X	0	0	0
Heat from decomposition of resin	X	X	?	X	X	X	X
Low vessel wall heat-transfer coefficient	X	X	NA	NA	0	NA	X
Low thermal conductivity of resin	X	X	X	X	X	X	X
Extraneous materials acting as catalysts	?	?	X	?	X	?	?
Extraneous materials: organic matter and/or resin extract	?	?	0	0	X	0	X
Large resin volume§	0	X	X	NA	0	X	0
Resin in nitrate form	X	X	X	X	X	X	X
Material contact time more than 1 hr	X	X	X	NA	X	X	X
Prior treatment with $>7N$ HNO_3	X	X	X	NA	0	0	X
Metallic ions loaded on resin	X	X	X	X	NA	0	X
System closed	NA	X	NA	X	?	0	0

*Meanings of symbols: X, present at time of occurrence; ?, possibly present; 0, not present; NA, information not available.

†Poor blending suspected.

‡$LiNO_3$ instead of HNO_3.

§Exact definition uncertain; for example, resin volume in the 7-cu ft vessel of Occurrence 6 is called "large volume," whereas that (2.88 cu in.) in the column in Occurrence 4 is termed "small volume."

These two incidents were mentioned by Kunin.[22] In one case an acid–base reaction was obtained when a weakly basic resin was contacted with strong HNO_3. Charring of the resin resulted. In the other case uranium was being recovered using a strongly basic resin. With an oxidizable material (polythionate) on the resin, the resin was being eluted at high temperature with a solution containing NH_4NO_3 and HNO_3. Nitrogen oxide fumes were liberated during the operation, apparently as a result of oxidation of the polythionate by the HNO_3. No damage to the resin occurred, but the resin apparently did play an indirect role in concentrating the polythionate.

Precautionary Measures Associated with Using Resins

All the precautionary measures given for ion-exchange resins in the accounts of the studies and incidents are listed in Table 3. The measures are divided into two groups: Group A measures are those associated with the chemistry of the resins, and Group B measures are general safety procedures for chemical processing. As a result it may be seen that many of the measures are not peculiar to using ion-exchange resins but are measures common to all safe chemical processing. In fact, it may be contended that all the measures listed in Group A are also general safety precautions that might fall under the category of knowing the chemistry of the process completely before starting to use it. Although this sounds like good advice, it does not seem to be generally followed in the area of safety, as is clearly shown by these seven occurrences.

The measures in Table 3 are listed in probable order of usual importance. The measures in Group A are generally preventive in nature. They are probably interdependent in that none can be used with safety to the exclusion of the others. The specific system in use should be studied to determine under what set or sets of these measures operation would be safe. Special mention should be made regarding the drying of resins (A-1) because the available information indicates that unpredictable results were obtained when resins were dried and/or heated. Van Slyke[16] reported that it was very difficult to get the resin dry enough to burn. However, Molen[19] found that the

Table 3 PRECAUTIONARY MEASURES RECOMMENDED IN THE USE OF RESINS*

A. Measures Associated with the Chemistry of Resins†

1. Avoid drying of resin (both in use and storage).
2. Consider dark-brown areas as danger signals that possibly indicate nitration of resin.
3. Observe predetermined safe temperature limit.
4. Observe predetermined safe HNO_3 concentrations.
5. Add sulfamic acid to nitric acid solution to react with nitrite-ion impurity.
6. Observe predetermined safe contact time limit between resin and specified concentration of HNO_3.
7. Limit ionic loading to predetermined safe value.
8. Avoid extraneous ions and materials.‡
9. Limit prior treatment to one predetermined to be safe.
10. Consider special precautions when transporting resins.

B. Measures Generally Applicable to Safe Chemical Processing§

1. Provide pressure-relief valve on column to avoid rupture.
2. Limit size of column to predetermined safe size.
3. Provide adequate blending of all HNO_3 solutions.
4. Monitor concentrations of all streams.
5. Monitor temperatures in column.
6. Provide high-temperature alarm so that column is flushed internally with water when alarm sounds.¶
7. Observe predetermined precautionary measures when equipment stands idle.
8. Vent column when not in use.
9. Limit amount of radioactive materials processed to predetermine safe values.
10. Improvise cautiously and with adequate protection during trouble.
11. Follow tested procedures.
12. Have adequate cleanup during and following maintenance.
13. Provide an external column flush.¶
14. Install mechanism (such as an agitator) to minimize risk of forming stagnant air pockets in column.
15. Regenerate resin with a continuous flow of HNO_3 to dissipate some of heat of reaction outside of column.
16. Limit size of resin to predetermined safe size.
17. Provide good heat transfer from column by internal cooling coils or external cooling jacket.

*Listed approximately in order of descending importance.
†In the absence of definitive tests for the specific situation, the various specified safe limits are unknown and cannot therefore be stated.
‡That is, by using pure water and by eliminating contaminants.
§As for the measures in Group A, values or limits would need to be determined for the specific situation being used.
¶Subject to limitations necessary to make the system safe from criticality.

liquid content of the resin affected the magnitudes of the ignition temperature and pressure directly and the maximum temperature and pressure during the subsequent disruptive reaction indirectly. Tests[23] made at a third laboratory in which Dowex 1 resin, both with and without radioactivity, was heated in an oven produced inconsistent results. In some cases explosions occurred at temperatures as low as 140°C; in other cases the resin simply charred on heating. From the evidence available the drying of ion-exchange resins must be viewed as potentially very dangerous and unpredictable—an operation to be avoided without adequate prior experimental work to ensure reliability of the results obtained. This warning is especially directed at the experimenter or health physicist who wants to dry a spent radioactive resin in order to determine its residual alpha and beta activities.

Disposal of spent resin was not mentioned in the studies. At one laboratory,[23,24] no trouble was experienced in disposing of spent resins by washing three times with a 25% solution of NaOH and four times with a 2% solution of Na_2CO_3 prior to packaging and storing. Each wash was followed by filtration. Two types of surve lance of these resins revealed (1) no pressure buildup, as determined by a pressure gauge, and (2) no change on periodic visual inspection.

Special mention should also be made of dangers in transporting used resins (Table 3, Item A-10) because no regulations specific to ion-exchange resins are available.[25,26] When shipping a used resin, a temperature alarm and pressure relief should be available, and provisions should be made to prevent drying of the resin.

The more important measures in Group B (1–11) should be rigidly adhered to. As nearly as possible, foolproof devices should be used. The pressure-relief device should preferably be a frangible disk instead of a type that might malfunction. The characteristics of the devices should be such as to produce the desired results *in the system being used.* For example, the pressure rating of the frangible disk and the size of the line containing it should be sufficient to give the needed degree or pressure relief. Van Slyke showed that pressure relief was quick and effective in reaction quenching *in every experiment*, even when test pressure had climbed to well above 300 psig (Ref. 16, p. 6). In addition, the response time of the temperature alarm and the rate of flow of the associated water flush should be capable of quenching the reaction produced by the maximum credible accident. Similarly, dilution and blending of acids should be carried out in batch tanks rather than by means of mixing valves, and concentrations should be checked before use; such

precautions would probably have prevented Occurrences 5 and 6.

Some of the minor measures in Group B also merit discussion. Providing good heat transfer from the column (B-17), for example, is of some benefit, but relying on it is a case of treating the effect rather than the cause. Good heat transfer from the column can be achieved by an external heat exchanger or internal cooling coils to dissipate the heat of reaction. It is certainly better, however, to prevent an incident by not exceeding the known maximum temperature limit than to attempt to stop the incident after it happens. Limiting the resin size (B-16) also seems relatively unimportant, since the resins are generally used in fairly small sizes anyway, and any size limits may be imposed by other considerations, such as the difficulty of holding a fine resin in place. Although an external flush (B-13) is essentially curative rather than preventive, it is a poor means of quenching a reaction inside the column upon indication of high temperature because of poor heat-transfer conditions. An ion-exchange column with stagnant air pockets (B-14) will certainly be less efficient than one without them.

The efficacy of the only known system with a high-temperature alarm interlocked with a water-flush and resin-dumping mechanism, now in operation at Mound Laboratory, has not yet been tested because the alarm has never been actuated by a real situation. In fact, no trouble with an uncontrollable reaction has ever occurred in an ion-exchange column at that installation. This indicates that safe operation can be realized in using the nitrate-form resin to process actinides (recovery of ^{238}Pu from waste streams) in about 7*N* HNO_3 (Ref. 23).

Potential Resin-Explosion Hazards in Reactor or Waste-Handling Facilities

The possibility has been considered that radioactive decay of fission-product iodine may overheat charcoal filters in a reactor ventilation system in a loss-of-coolant accident. The potential conditions have been analyzed, and steps have been taken to prevent undesirable results. Apparently no similar investigations have been considered, however, of the correlative possibility of demineralizer resin overheating following inadvertent release of large amounts of highly radioactive material into a reactor cooling system. A concomitant question would be whether failure of the letdown cooling system, which reduces the temperature of power-reactor cooling water from 550 to 100+°F prior to its entry into the demineralizer resin beds, might result in sufficient heating to set off a resin explosion.

A specific instance of a potential pathway for resin to reach unexpected locations outside the normal resin system was discovered recently at the 50-Mw(e) boiling-water reactor at La Crosse, Wis.[27] On Feb. 2, 1968, La Crosse operators attempted to sluice anion resin from the condensate demineralizer service tanks to the regeneration tank and found the first service tank to be empty down to the takeoff line. Fourteen cubic feet of resin was finally determined to be missing from the service tanks; it had been inadvertently discharged to the waste lines sometime previously, apparently during automatic regeneration. Fortunately the resin was in the hydroxyl form and thus caused no untoward effects; it was eventually discharged safely from the waste system. Had it been a nitrated resin, the story might well have been different.

A similar incident, of a relatively minor nature, was reported on Oct. 21, 1966, at Mound Laboratory.[28] "A small quantity of plutonium 238 was released when a double-contained vessel, nearly full of drybox-sieved material intended for recovery of the isotope, exploded and dispersed a quantity of the material in a laboratory. It was suspected that some nitrated anion resin, which is unstable to heat, especially when dry, found its way into the waste material through normal drybox cleaning activities . . . ." No personnel radiation exposures resulted, and the decontamination cost was $19,100.

These occurrences point out the necessity for considering possible mechanisms by which nitrated anion resins might reach unexpected locations in the waste system, perhaps during normal operations, or regeneration, or in resin transfer prior to disposal (dryout), and become explosion hazards.

Conclusions

Two ideas associated with safety measures deserve special mention. First, it should be noted that all the occurrences took place through self-ignition of nitrate-form resins. It is also noteworthy that, under the conditions used in the studies, the nitrate form was the only form that exhibited self-ignition. This, of course, does not mean that other forms of resins will not undergo self-ignition under other conditions, but it certainly does indicate that the nitrate form at least deserves special study and precaution. Second, the mechanisms through which trace elements or catalysts promote self-ignition of resins are unknown. The catalyst may even be a trace of inorganic material in the organic resin; that is, the inverse of the case in which a trace of organic material is the catalyst in the ignition of inorganic ammonium nitrate. This is an insiduous factor in that the presence of such materials is usually not known, and therefore the cause of an explosion or other incident may never be known. Such a factor certainly indicates the necessity of extreme cleanliness when working with ion-exchange resins, including initial startup under clean conditions and frequent replacement of tubing.

This discussion of precautionary measures has purposely been made general because of the many resins on the market and because resins vary in behavior, even from lot to lot of the same resin. However, the measures given identify areas of possible difficulty. Therefore experimental work to establish safe limits in these areas before using a given ion-exchange system should be considered mandatory.

It should be obvious that the increasing usage of ion-exchange resins in laboratory and pilot-plant-scale processing of actinides deserves more safety study, if for no better reason than the prevention of just one incident which would probably return the money expended in the entire study. For example, previous studies have been restricted, in some cases, to small-scale experiments on a few grams of material. No tests were made of the consequences either of a sudden increase in water temperature to 550°F in a reactor ion-exchange resin bed or of the massive release of fission fragments concentrated in the reactor coolant demineralizer.

The effects of radioactive species on nitrate-form resins in strong HNO_3 have not been investigated thoroughly. Although gamma radiation is known not to initiate detonation in aromatic nitro compounds,[29,30] it does produce reactive decomposition products such as oxides of nitrogen, hydrogen, nitrobenzene, benzene, and toluene.[31] Radiation does reduce the retention capacity of an ion-exchange resin, depending on the specific resin and the amount of radiation. Information from the Radiation Effects Information Center at Battelle Memorial Institute revealed that (1) radiation breaks the cross-linkages of ion-exchange resins[32] and degrades the functional groups of quaternary amine anion resins,[33] (2) the N^+Me_3 ion-exchange groups are relatively easily split off from strongly basic resins of polystyrene during irradiation,[34] and (3) the radiation of the nitrate form of quaternary strong base (styrene) resins probably produces such unstable species as amines (especially Me_3N) and the nitrite ion.[35–37] For plutonium solutions containing high levels of fission products, the major factor in degradation is the high beta–gamma activity; for low levels of beta–gamma activity, the alpha activity of the absorbed plutonium will be an important factor in the degradation.[5] In some of the incidents described, the concentration of alpha emitters was fairly high, and the local concentration of decomposition products might have been high enough to have lowered the so-called "critical temperature." However, attempting to generalize about the effects of radioactivity would be less productive than studying each system under its conditions of use.

Information on the safe processing of actinides with anion-exchange resins in a nitrate system has come primarily from the five studies cited[1,3,10,16,18,19] and from the practices at Mound Laboratory.[23] The Chemical Rubber Co. "Handbook of Laboratory Safety," however, contained no data on safety in using ion-exchange resins.[38] Prior to the five studies cited, information on resin stability in processing plutonium was directed specifically to the loss of capacity through chemical, physical, and radiation damage.[5] General information on resin stability was directed to resin degradation, loss of capacity, and fouling.[4] Manufacturers' information on safe resin handling was limited to physical expansion and heat evolution on wetting the resin, to decomposition when the resin dries out, and to decrepitation under alternate conditions of freezing and thawing. One manufacturer disclaimed responsibility for difficulties a user might encounter by recommending that the prospective user determine the suitability of its materials and suggestions before adopting them on a commercial scale.[39] This is a reasonable position, *but the warning should be specific, the information provided should be adequate, and the user should be fully aware that the manner in which he utilizes the materials and information is clearly his responsibility.*

Finally, it is apparent that (1) nitrate-form anion-exchange resins are potentially dangerous whether being used to process actinides or not, and (2) the user of such resins should, before use, thoroughly evaluate the safety of the anticipated conditions of use. Guidelines for such an evaluation are set forth in the text and summarized in Table 3. (PSB)

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MEDICAL SUPERVISION OF RADIATION WORKERS

Safety Series No. 25, IAEA, Vienna, 1968

By H. Jammet (France) and F. Herčik (Czechoslovakia)

In 1960 the IAEA published a manual, *Safe Handling of Radioisotopes: Medical Addendum*, which was No. 3 (STI/PUB/11) in its Safety Series. The writers of the new booklet, which is a revised edition of the Addendum sponsored by IAEA, ILO, and WHO, collaborated in writing the original edition. *Medical Supervision* provides information for implementing the controls in the main manual [Safety Series No. 10 (STI/PUB/44)] and an introduction to technical problems of radiological protection. Subjects covered are basic concepts, radiological hazards, radiation protection standards, and health supervision. 25 references. Available in both English and French editions. (MG)

Section
VI
Isotopes and Radiation Technology

Isotopes Around the World

Some Possible Contributions of Radioisotopes in Meeting Emergent Africa's Basic Needs

By J. R. Stebbing*

"Emergent Africa" is taken as the region lying south of the Sahara and north of the Republic of South Africa. It is inhabited by more than 200 million people, who are increasing at a rate of more than 4 million each year and live in 33 separate countries, most of which are newly independent. The purpose of this study is to identify some of the grafting points in the general framework of development where radioisotope techniques might most profitably be used. The principal fields considered are: seed improvement, improved use of fertilizers, pest control, grain disinfestation, and groundwater tracing.

Seed Improvement

Improvement of rice seed has been achieved by radiation-induced mutations, particularly valuable work having been done in seven countries of Southeast Asia (Ceylon, China, India, Japan, Pakistan, the Philippines, and Thailand). This has been done under a joint Food and Agriculture Organization–International Atomic Energy Agency (FAO–IAEA) project and a program of the International Rice Research Institute in the Philippines. Work in Japan resulted in mutant lines of rice reaching maturity up to 50 days earlier than the mother variety, so that an extra crop each year has become possible.[1] China has reported the results of four mutant lines with 3 to 8% greater yields and greater straw strength than local varieties.[2] Work in India has resulted in improved grain, higher yields, and disease resistance. Steps have been taken to organize trials in all seven participating countries to compare the mutants with local and internationally known varieties. Africa needs research support of a similar kind to develop new strains of maize and millet.

Improved Use of Fertilizers

The efficient use of fertilizers has been studied with an entirely new degree of precision by means of radioactive tracers, which can be chemically associated with their stable phosphorus or nitrogen counterparts in a fertilizer. Using these tracers, different methods and timing of fertilizer applications can be studied with a speed and precision that have never before been possible. Recent experiments on fertilizer applications in Asia and the Far East, in a number of countries with widely differing soils and climates, have given consistent results.[3] For example, broadcasting of fertilizers on the surface of the soil is found to be practically as effective as the far more costly process of working them in, and late application of fertilizers can be effective. Fertilizers can beneficially be broadcast even over growing rice, and thus vagaries of supply in remote areas need not jeopardize crop yields, as they have done in the past. By conducting identical and simultaneous experiments at widely separated points, work has been done in 1 year which might have taken at least 5 years by traditional methods since the conclusive results obtained could be immediately applied in practice.[4]

*UKAEA Research Group, Culham Laboratory, Abingdon, Berks., England; based on UKAEA Report CLM-P 138. Mr. Stebbing was for 24 years a member of the British Colonial Administrative Service in West, South, and East Africa. For 10 years he was involved in economic planning. Since retiring from the Colonial Service in 1959 he has held administrative posts in the UKAEA.

Comparatively little work of this kind has been done in Africa. However, in one experiment in a Congo oil-palm plantation, fertilizer-uptake measurements showed[5] a 10 to 20% decrease in the amount of fertilizer used and a 75% decrease in application costs when the fertilizer was broadcast, compared with uptake and cost when it was mixed with the soil. Fertilizer trials with maize have been started in Argentina, Brazil, Colombia, Mexico, and Peru.[6] Once again, similar studies are needed in Africa with both maize and millet.

Pest Control

Pest-control investigations in the Far East and Asia have been a part of the measures to improve rice production.[7] The stem borer, the principal threat to rice crops at every stage of growth, can be controlled by insecticides; but these are costly and in some degree indiscriminate, they must be applied more than once, and they can involve the handling of hazardous chemicals. Investigations are now under way to control the stem borer by the sterile-male technique, using ionizing radiation. This is a vast task with obvious difficulties, but there is the possibility of very significant and lasting improvements in food production.

Africa has more than its share of pest problems. The tsetse fly profoundly affects life in a million square miles of the continent. It threatens human life directly and severely decreases cattle production and the benefits that cattle husbandry can bring. It has been known for 10 years that the tsetse fly is one of the few species that might be eliminated by releasing males, sterilized by nuclear methods, in sufficient numbers to reduce the reproduction rate of the fly to below survival level. This possibility is being explored in Uganda; it should also be considered throughout the very large tsetse-fly areas stretching from Nigeria to southern Tanzania. This is an immense task that would call for very close interterritorial collaboration, as well as outside help.

Grain Disinfestation

African grain losses due to insect infestation are frequently as high as 25%, and percentages of double this figure are not unknown. Storage in many areas has not changed from the primitive tribal methods, which provide very little protection against vermin and less against termites. Storage is traditionally a short-term matter, because production is barely sufficient and margins are precarious. But food-grain surpluses are now beginning to appear in East and Central Africa in areas of better developed communications. For these, the recent advances in grain disinfestation could prove of great value.

The Nuclear Chemical Plant Ltd. of London has designed a small Mobile Grain Irradiator [costing £13,000 ($30,000)]. It could be moved by a 10-ton truck and could handle up to 1 ton of grain per hour. It is based on a well-tried research irradiation unit of robust design, suitable for transportation.[8] This process awaits the completion of wholesomeness tests before it can be employed. In the meantime, advances are being made in storage methods, some of which are inflatable containers and, possibly, grain bags of new materials that prevent reinfestation.

Groundwater Tracing

Radioactive isotopes can be used in tracing groundwater with some advantages over the soluble dyes used in the past. Soluble ^{131}I compounds, for example, are less easily removed from the water than are the dyes, and they are detectable at short distances from the surface so that instantaneous quantitative measurements are possible in situ.[9] These compounds are particularly suitable for the porous strata so prevalent in Africa, where water moves in open passages. Tritium can also be used as a constituent part of the water itself; it is not leached away and can be used in the least porous soils. However, there are technical difficulties with it, and only a limited number of samples can be assayed per day.

These two methods offer possibilities of water tracing, particularly in arid zones where little is known of underground water movements and where it would be of great value to discover the routes followed by water from river spates between the points at which they go underground and their ultimate areas of storage. Although these zones are not highly populated and their peoples are often nomadic, they could not be absorbed elsewhere, and the first requirement for improving their condition is to provide reliable water supplies.

In Asia, populations are far greater than in the African countries and, although the degree of Asian poverty is little different, the national research effort is sufficient in scale to embrace nuclear science. This is not so in Africa where the benefits of nuclear science will only become available by international effort, largely from outside.

Africa needs research support to improve food and water supplies and to eliminate the tsetse fly. The

benefits could be very great. By improving crop yields and eliminating storage losses, food-grain resources could be more than doubled. The removal of anxieties about basic needs of food and water would help to stabilize African society and release energies for promoting economic and social advances in other fields.

(MG)

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The Radiochemical Centre, Amersham*

Radioactive work began at Amersham in April 1940, with the refining of radium and the manufacture of luminous paints for the wartime aircraft industry. It was a venture of private enterprise, with a small laboratory working under technically primitive conditions, equipped with few instruments, and staffed by no more than a dozen people—but this was the nucleus around which later developments were built.

The Radiochemical Centre was established under public ownership on the same site in 1946. Its purposes were quite definite: to provide radioactive substances, however and wherever they might be needed by doctors, engineers, and research workers, at home or abroad—and to do so in a businesslike way as a commercial enterprise.

The purposes of the Centre are the same today, but its technical resources have grown immensely. The basic raw materials are derived from research reactors at Harwell and from several production reactors elsewhere within the United Kingdom Atomic Energy Agency (UKAEA), thus providing a highly dependable service. There are extensive laboratories, well-equipped for all kinds of radioactive work. A powerful cyclotron has recently been installed, the first machine of its kind to be designed and operated solely for making radioisotopes.

The range of radioactive products available from the Centre has grown to an extent that would have been unbelievable 20 years ago in the age of radium. The current catalog offers some 2000 items. There are 150 radioisotopes available in more than 1000 chemical compounds and in 600 to 700 kinds of radiation appliances. Standards of quality and purity are extremely high, to meet many specialized uses in medicine, industry, and research.

The Centre now employs 500 to 600 people. In 1966–1967 nearly 75,000 consignments of radioactive products were sent out, to almost every country in the world. (MG)

*Reprinted from *Atom*, No. 142, pp. 217-218 (August 1968).

Section

VII

Isotopes and Radiation Technology

Miscellaneous

Availability of Isotopes and Services

ORNL Stable-Isotope Inventory Augmented

Recent additions to the ORNL enriched stable-isotope inventory include the following:

Isotope	Purity, %	Amount available, g
^{46}Ca	35.4	0.148
^{46}Ca	40.9	0.149
^{63}Cu	99.7	478.5
^{65}Cu	99.7	157.7
^{104}Pd	89.7	2.2
^{148}Sm	96.4	50.7
^{149}Sm	97.7	68.8
^{150}Sm	95.5	37.8
^{154}Sm	99.5	75.4

(PSB)

Accelerator Services Offered

Midwest Irradiation Center, Inc. (301 S. Water St., Rockford, Ill. 61104), is offering the services of its 12-Mev Arco linear electron accelerator for small and large production runs, pilot studies, and experimental work. Midwest was formerly a subsidiary of Electronized Chemical Corp. but is now an independent Illinois corporation.

Sherlock: New Isotopic Neutron Source for On-Line Activation Analysis

A new on-line instrument, utilizing neutron activation analysis, has been designed by Atomic Energy of Canada Ltd. Commercial Products and is expected to be commercially available within 6 months. "Sherlock I," named for the fictional detective, is a 15-ton unit intended for in-plant installation and will be the first commercial on-stream application using neutron activation analysis. The radiation source is ^{124}Sb–Be with a flux of 2.0×10^8 n/(cm^2)(sec). The irradiation facility will be equipped to handle process flows from 0.5 to 8 gal/min. In developmental work the most efficient flow rate for most elements has been in the 1- to 3-gal/min range.

Offered initially for one stream at a time, the irradiation chamber can be modified to accept three or four streams simultaneously. Provision can also be made for recycling of a stream in a closed loop to increase the sensitivity if the required analysis time for a particular process is, say, half an hour. The average analysis time of 5 to 15 min has been found adequate for most processes.

A possible future model, "Sherlock II," would most likely have a uranium sleeve over the Sb–Be source to convert the thermal neutrons to fast neutrons, thereby enabling the unit to determine some elements that Sherlock I cannot detect, e.g., S, Fe, Si, and Zn.

Training in Radioisotope Use

Radiopharmacists

The School of Pharmacy, University of Southern California, announces the establishment of a new program leading to a *Master of Science in Radiopharmacy*. This program is a pilot program, and the first and only one of its kind in the nation. It is under the direction of Professor Walter Wolf, with the codirection of Professor Manuel Tubis. The program has been made possible by a grant from the Bureau of Health Manpower, Public Health Service, after several surveys had shown the great need for radiopharmacists. No such persons are being trained currently. The pro-

gram at U.S.C. intends to train 10 highly qualified individuals annually. The program is open to all qualified pharmacists with the appropriate background and consists of three semesters' work: (1) study of basic sciences (physics, chemistry, biology, synthesis, and metabolism of radionuclides); (2) study of applications (health physics, dosimetry, radiopharmaceutics, and nuclear medicine); (3) residency in a center of nuclear medicine. For further details contact Professor Walter Wolf, Radiopharmacy Program, School of Pharmacy, U.S.C., Los Angeles, Calif. 90007.

Science Teachers

The Atomic Energy Commission and the National Science Foundation (NSF) will sponsor 36 faculty training institutes to accommodate 800 high school and college science teachers, in nuclear science during 1969. These institutes, which will be conducted by selected colleges and universities and two AEC laboratories, provide graduate level work, which will help those enrolled teach nuclear science in their own classrooms. Subjects covered will be radiation biology, radiochemistry, radioisotope techniques, and nuclear physics.

AEC and NSF together fund the total cost of the institutes. AEC generally provides operating expenses, including faculty salaries for those teaching the courses and the costs of using school facilities. NSF makes money available for travel and to pay small stipends to teachers enrolled in full-time institutes. General information about AEC–NSF institutes may be obtained by writing the Division of Nuclear Education and Training, USAEC, Washington, D. C. 20545 or the National Science Foundation, Washington, D. C. 20550.

Environmental Research Program in Terrestrial Ecology

The Department of Environmental Engineering, University of Florida, Gainesville, has announced a continuing program of environmental research in tropical and subtropical terrestrial ecosystems. Because of the basic and interdisciplinary nature of the investigations, results will be applicable to agricultural, biological, ecological, environmental, and nuclear research. Element concentrations are to be determined in defined compartments while the ecosystems are in dynamic equilibrium; input and outflow of elements through the specific ecosystems will be investigated; and cycling of specific elements within an ecosystem will be followed by introducing radiotracers at concentrations slightly above background radiation levels. Activation analysis is available for special determinations and as an absolute method. Special, low-level radiochemistry facilities include two gamma-ray spectrometers, low background beta systems, liquid scintillation spectrometers, and complete sample preparation facilities.

Research topics at the master, doctoral, and postdoctoral level are available. Qualified students interested in pursuing graduate research within this program should contact the Terrestrial Ecology Research Program, Department of Environmental Engineering, University of Florida, Gainesville, Fla. 32601.

(RHL and MG)

AEC Activities

ORNL Prepares Large ^{90}Sr Sources

The Oak Ridge National Laboratory's Isotopes Development Center has recently completed the preparation and encapsulation of radioactive strontium titanate fuel for use in advanced versions of thermoelectric-power-generator devices. An 1100-watt(t) source, the largest single radioactive strontium fuel capsule ever assembled, is for use in a SNAP-23 system being developed for remote terrestrial applications. The total amount of heat produced by the 13.5 lb of fuel in this source over the next 10 years will be equal to that produced by burning 15 thousand lb of fuel oil. Four 200-watt(t) sources were made for use in SNAP-21 power conversion systems, which are being developed for deep-sea and ocean-bottom use at depths down to 20 thousand ft. The ^{90}Sr used in the sources was recovered from the waste from spent nuclear fuel processing and chemically processed to strontium titanate powder, which was hydraulically compacted to very dense pellets. A SNAP-21 ^{90}Sr titanate generator developed by 3M, which is to be tested on the Pacific Ocean floor, near Los Angeles, is designed to produce 10 watts(e) for 5 years without refueling.

A source plaque consisting of ^{90}Sr silicate microspheres in an aluminum matrix and clad in stainless steel has been developed for use by Brookhaven National Laboratory (BNL) in its ^{90}Sr studies (see below).

Oak Ridge Radioisotope Shipments Total 2965 in 1968

The USAEC's Oak Ridge National Laboratory made 2965 shipments of radioisotopes, representing 3,647,774 curies, in 1968. Following a recent trend, the total number of shipments was down from the previous year's total of 3956 because of a continuing policy of the AEC to turn over the routine production and distribution of many radioisotopes to private industry. The 1968 curie total remained high—only slightly less than the record high curie total of 3,669,646 in 1967—because of the higher specific activity and larger individual orders of certain radioisotopes which the Commission supplies for research and special industrial applications. The bulk of the 1968 curie total was represented by four radioisotopes—^{90}Sr, used in the fabrication of isotopic power sources; ^{3}H, used for production of labeled compounds and luminous products; and ^{60}Co and ^{137}Cs, used in process radiation applications and research.

USAEC Radioisotope Licensing Changes

Smoke Detectors

The AEC is proposing a new class exemption from licensing for radioisotopes in smoke detectors and other gas and aerosol detectors designed to protect life or property from fires and airborne hazards. In the past, smoke detectors containing radioisotopes have been used under general or specific license. Under the new proposal, such detectors which meet specific safety standards would be exempted as a class from further regulatory control. Manufacturers would continue to be licensed. The proposed amendments would provide flexibility for selection of a radioisotope by the manufacturer and minimize regulatory restrictions on his development programs.

A manufacturer seeking a license to distribute such detectors would be required to submit results, from prototype tests, which demonstrate that the exempt detectors would adequately contain the radioactive material and radiation under both normal and the most severe conditions of handling, storage, use, and disposal. To ensure that the detectors would not endanger public health, the Commission would also require details on estimated radiation exposure. The proposed rule responds to petitions received by AEC from manufacturers seeking exemptions for smoke detectors containing ^{241}Am, ^{63}Ni, and ^{232}U. Detectors containing ^{85}Kr and ^{3}H are under development.

Details of safety standards and information required from manufacturers can be found in the proposed amendments to Parts 30 and 32, which have been transmitted to the *Federal Register.*

Electron Tubes

The AEC is considering amendments to its regulations (Parts 30, 31, and 32) to exempt from licensing the use of radioisotopes in electron tubes. The exemption would be limited to electron tubes containing specified small quantities of ^{3}H, ^{60}Co, ^{63}Ni, ^{85}Kr, ^{137}Cs, and ^{147}Pm. The present general license for spark-gap tubes containing some of these by-product materials would be revoked. The proposed rule responds to petitions from manufacturers seeking exemption for tubes containing these radioisotopes.

The manufacture or import of tubes containing these radioisotopes would continue to require a specific license. Regulations applicable to holders of such licenses would be revised to exempt the tubes from the requirement for visual inspection and to add a requirement that the tubes (as well as most other products containing radioisotopes used on an exempt basis) be labeled to allow identification of the manufacturer or importer and the radioisotope involved.

Iodine-125

Proposed changes [*Isotopes and Radiation Technology,* **6**(2): 218] in AEC regulations, which would eliminate the need for physicians, clinical laboratories, and hospitals to have a specific license for in vitro use of ^{125}I in small amounts, have been implemented. The changes became effective 60 days after publication in the *Federal Register* on Nov. 14, 1968.

AEC Amends Transportation Regulations

The AEC is amending its regulations on the safe transportation of licensed radioactive material to bring them into conformity with a new revision of Department of Transportation (DOT) regulations. In 1966 the regulations were revised to incorporate performance standards for shipping containers and for packing and

shipping ^{233}U, ^{235}U, and plutonium as well as for large quantities of other licensed radioactive material, such as radioisotopes. In April 1967 the regulatory authority of the Interstate Commerce Commission relating to safety in transport was transferred to the DOT, which, in January 1968, published a proposed major revision of regulations. The DOT published its revised regulations in effective form in the *Federal Register* on Oct. 4, 1968, and the AEC is now making the necessary changes to bring its regulations into conformity. The most significant change in AEC rules relates to the number to be placed on the label of fissile material packages for nuclear criticality safety control. The amendments to AEC Part 71, "Packaging of Radioactive Material for Transport," became effective Dec. 31, 1968.

Brookhaven National Laboratory To Evaluate ^{90}Sr Sources

The High Intensity Radiation Development Laboratory (HIRDL) at Brookhaven is about to begin evaluation of ^{90}Sr for the USAEC's Division of Isotopes Development. The studies will be designed to show whether this radioisotope as the silicate is useful for large-scale beta-radiation applications, such as the processing of foods or plastics, or in radiation-chemical processing. About 60 thousand curies of ^{90}Sr as $SrSiO_3$ mini-beads in an aluminum matrix will be prepared by ORNL and encapsulated in thin-walled rectangular stainless-steel tubing for use as the radiation source. Approximately 5 thousand curies of ^{90}Sr were recently delivered to BNL.

A long-term source-geometry and dose-distribution program on ^{60}Co which has been under way for some time is now tapering off, but a ^{137}Cs program is still being pursued. Some 300 thousand curies of ^{137}Cs, in three portable irradiators, will be loaned by AEC to Argentina, Chile, and India for food-processing studies. These irradiators were built to AEC specifications by Radiation Facilities Inc., Lodi, N. J., and Stewart Glapat, Zanesville, Ohio. A 30-thousand curie ^{60}Co pool-type irradiator for research will be sent to Pakistan this spring.

Sewage Treatment with Ionizing Radiation

Thirty-three proposals were submitted to USAEC for economic and technological evaluation of the use of radioisotope sources in sewage processing. A contract was awarded to Gulf General Atomic Incorporated of San Diego, Calif., and the work will be under the direction of Dr. D. M. Compton.

In Canada the Atomic Energy of Canada Ltd. Commercial Products group has provided Gammacells—one using 4800 curies of ^{60}Co and the other 236 curies—for the study of sewage treatment. The work is being done by the Ontario Water Resources Commission, which is using much lower doses of radiation than the 100 thousand rads under study by the Metropolitan Water District of Greater Chicago. The higher doses are reported to facilitate water removal from the sludge and thus cut sludge haulage costs.

Radiation Used in Efforts To Develop New Concrete–Plastic Materials

Atomic Energy Commission and Bureau of Reclamation scientists are developing an improved type of concrete by using radiation to combine conventional concrete and plastic. Samples of the new material, called "concrete polymer," test four times stronger than ordinary concrete, according to a newly published research report, available to the public.* The process and the material are being developed at AEC's Brookhaven National Laboratory at Upton, Long Island, under a Division of Isotopes Development (DID) contract. Sample preparation and final product testing for this joint agency effort are being conducted at the Bureau of Reclamation's Engineering and Research Center in Denver.

Ordinary hardened concrete made of cement, water, and aggregate is placed in a vacuum and then soaked in a liquid monomer, e.g., methyl methacrylate. When this impregnated concrete is exposed to ^{60}Co gamma radiation for several hours, the liquid polymerizes to a plastic. The monomer may also be polymerized by a combination of heat and radiation or of heat and chemical catalyst.

Interconnecting voids make up about 14 vol.% of ordinary hardened concrete. This allows thorough impregnation by the monomer, which upon polymerization results in four times more tensile and compressive strength. Because the voids are filled with polymer, water permeability is reduced to a negligible level, and thus resistance to freeze–thaw deterioration is in-

*Concrete-Polymer Materials, First Topical Report, Brookhaven National Laboratory, USAEC Report BNL-50134 (Department of the Interior's Bureau of Reclamation and Office of Saline Water as USBR General Report 41), 1969. CFSTI, $3.

creased. Abrasion and cavitation resistance is four or five times greater. The depth of the penetration of the plastic into the concrete can be controlled. Complete penetration increases the weight of the material less than 7%.

The concrete-polymer material is being evaluated for use in desalting plants. The Office of Saline Water is particularly interested in the material's resistance to deterioration by brine and distilled water at temperatures as high as 290°F. Interest in possible applications has been shown by other federal agencies, including the Naval Civil Engineering Laboratory, the Army Corps of Engineers, the Department of Agriculture's Research Service, and the Bureau of Public Roads.

How To Get a License To Use Radioisotopes

A 35-page booklet, issued in July 1967 by the Division of Materials Licensing of the U. S. Atomic Energy Commission, tells the prospective user of radioisotopes how to get a license. The booklet explains in nontechnical and nonlegal terminology the objectives of the regulatory program, how it functions, and the safety responsibilities of persons who use radioisotopes. It is available from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, for 30 cents.

"Sea Gulliver" Developed

An instrument named the "Sea Gulliver" has been developed by Biospherics Research, Inc., of Washington, D. C., under contract from the Atomic Energy Commission as part of the AEC's effort to introduce isotope technology to industry. The device is a cylindrical instrument about 8 in. in diameter and 1 ft long for studying the lilliputian phytoplankton in an effort to decrease guesswork in commercial fishing.

The Sea Gulliver, like the "Space Gulliver" [described in *Isotopes and Radiation Technology*, 4(2): 108-110 (1967)], uses a radioisotope technique to measure growth of living organisms and is concerned with phytoplankton—the microscopic sea plants that grow by using the sun's energy, carbon dioxide, and water. Phytoplankton is the first link in the oceans' food chain. The small organisms are eaten by successively larger organisms and ultimately sustain the total fish population. A measurement of the rate at which plankton reproduce will provide an estimate of the food available to fish and, hence, the size of the coming fish crop.

The instrument is being designed for automated unattended operation under the sea to trap small samples of seawater and plankton in transparent containers. Radioactive carbon released into the sample will be incorporated into the plankton during normal photosynthesis. After several hours of growth, the plankton will be removed by filter and the incorporated radioactivity measured. The amount of plant growth which takes place can thus readily be calculated. Data obtained in the periodic tests will be stored in the instrument.

Isotope User's Guide Published by Isotopes Information Center

In the past, the Oak Ridge National Laboratory (ORNL) catalog of radioactive and stable isotopes has been requested many times by teachers, students, and other persons who were interested in using isotopes or who wanted information on isotopes. The catalog also contained much data on isotopes that regular users found helpful. The Isotopes Information Center has published a new booklet aimed at this audience.

The *Isotope User's Guide* (F. E. McKinney, S. A. Reynolds, and P. S. Baker, ORNL-IIC-19, May 1969) lists approximately 200 commercially available radioisotopes; the half-life, production methods, kinds of radiation, and energies and conversion percentages for the radiations are given for each isotope. Definitions of some of the scientific terms usually associated with physics, but also used with radioisotopes, are provided for new users. Some suggestions are offered in choosing an isotope for a specific use, and shipping information and descriptions of special irradiation services are included. Suppliers of small quantities of radioisotopes for classroom use are listed. An interesting feature is a tabulation by half-life of all 200 radioisotopes. There is a section on assay methods and on available standards. Information on the preparation, availability, and uses of stable isotopes is also presented.

The *Isotope User's Guide* is intended as a guidebook to isotopes for both experienced and new users, and, although it is based primarily on experience and practice at ORNL, it should be helpful wherever isotopes are used. Copies are available on request from the Isotopes Information Center, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tenn. 37830.

(FEM)

General

International Chemical & Nuclear Buys Tracerlab Interest

International Chemical & Nuclear Corp. has bought Tracerlab's name and 30% of its $10 million business. Approximately 100 employees will transfer to ICN with Tracerlab's radiochemical operations, lines of laboratory instruments and detectors, film-badge service business, and Belgian-based European marketing subsidiary. The acquisition provides ICN with significant foreign distribution channels. The ICN is already a leader in radiochemicals and has begun to develop a radiopharmaceutical line.

New York State Atomic Energy Council

Dr. Hollis S. Ingraham, State Health Commissioner, was elected chairman of the New York State Atomic Energy Council at its first meeting, held in Albany in December. Neal L. Moylan, State Commerce Commissioner, serves as executive secretary. A Committee of Licensing, consisting of representatives from the State Health, Labor, and Commerce Departments and a New York City representative, was also established.

The Council, which is composed of the chief officers of departments and agencies having important interests in atomic energy and the regulation and control of atomic energy activities, is the chief policy body of the State with respect to atomic energy regulatory and control programs. Its fundamental responsibility is to "assure that regulatory programs ... affecting atomic energy activities encourage the development and use of atomic energy ... while fully protecting the interest, health and safety of the public."

Radioisotopes in Pollution Tests

The International Atomic Energy Agency (IAEA) is planning studies on pollution in the Danube River. Neutron activation analysis for elements (e.g., mercury and arsenic), tracer studies on flow rates and sediment transport (using, e.g., ^{82}Br and ^{140}La), and radioisotope gaging will be among the techniques used.

New Contracts

Tyco Laboratories, Inc., has negotiated a $100,000 contract with the AF Flight Dynamics Laboratory for development of lightweight, compact, reproducible gamma-ray detectors for fuel gaging. Work would be done at the Research Division, Waltham, Mass. A second contract was awarded to Tyco's General Nucleonics Division, Claremont, Calif., by the AF Logistics Command, San Antonio Air Materiel Area, for retrofitting all F106A and F106B aircraft presently in service with the General Nucleonics' nucleonic oil gage. The size of the contract is being negotiated.

Susquehanna Corp. has obtained a $43,000 contract from the AEC for studying the use of isotopic radiation in combination with chemical treatment to increase the destruction of bacteria in sewage waste water. The primary purpose of the study is to determine whether an enhanced, or synergistic, effect in killing bacteria in waste water is achieved through a combination of isotopic and chemical means (^{60}Co and chlorine). If such a combination proves more effective than other means of treatment, the economic advantages of using isotopic radiation will be assessed.

Choosing Gulf General Atomic out of 33 proposers, AEC's New York Operations Office is negotiating a $100,000 contract for a study to determine the practicability of using ionizing radiation for treatment of waste water. The 10-month economic and feasibility study will involve an experimental program to acquire data, an evaluation for the possibilities of ionizing radiation, and preparation of recommendations for areas of radiation treatment to be used.

Westinghouse Astronuclear Laboratory has been awarded the first phase of a DID contract to design a 30-kw(t) ^{60}Co heat source. Four additional phases may follow, resulting eventually in a prototype heater with 2 Mc of ^{60}Co. The cost of the whole project could reach $1 million.

Canada Clears Irradiated Wheat

Irradiation of wheat and wheat flour for insect disinfestation has been cleared by Canada's Food and Drug Directorate. The United States has already cleared irradiated wheat and wheat products, and the USSR has approved insect disinfestation of grain, dried fruits, and dry food concentrates by irradiation. Canada previously cleared irradiated potatoes and onions, and the United States, Israel, and the USSR have approved irradiation as a means of inhibiting sprouting. There is a report that the Russians are designing fish irradiators for use on both sea and land.

Large-Scale Isolation of ^{147}Pm

Battelle–Northwest, Richland, Wash., recently announced the isolation of some 100 g of ^{147}Pm metal, the largest amount of this product yet made. The process used was conversion of the oxide, obtained from processing of nuclear-fuel-processing waste, to the chloride and reduction of the chloride with calcium and iodine. The 99.9% pure product has a density of 7.2 g/ml and a melting point of 1168 ± 6°C.

Conference on Process Radiation in the Plastics Industry

Washington State University, Pullman, Wash., and the Office of Nuclear Energy Development, Department of Economic Development, State of Washington, will sponsor a 3-day course in process radiation in the plastics industry in Pullman, Wash., June 11–13, 1969. This conference is scheduled just prior to the annual meeting of the American Nuclear Society in Seattle, Wash. (distance from Pullman to Seattle is 6 hr by car). The registration fee is $65 (preregistration $60). The program of the conference follows:

WEDNESDAY, JUNE 11, 1969

8:00 Registration

8:30 Welcoming Addresses
E. W. Greenfield, Director of Research, College of Engineering Research Division, Washington State University, Pullman, Wash.
Donald Fielding Koch, Executive Director, Office of Nuclear Energy Development, Department of Commerce and Economic Development, Olympia, Wash.

9:00 Keynote Address
Lawrence B. Bradley, Nuclear Energy Assistant, Office of Nuclear Energy Development, Department of Commerce and Economic Development, Olympia, on "Sell the Idea, Not the Source!"

Morning Session

R.A.V. Raff, Presiding
Washington State University,
Pullman, Wash.

9:30 "Fundamentals of Radiation Processing"—Course by V. T. Stannett, North Carolina State University, Raleigh, N. C.

Noon LUNCHEON
"Activities in the Chemical Research Section of the College of Engineering Research Division of WSU"—Speaker, Mark F. Adams, Washington State University, Pullman, Wash.

Afternoon Session

R.A.V. Raff, Presiding

1:30 Course by V. T. Stannett continued
4:30 Questions and Answers
6:30 No-Host Mixer
7:00 DINNER
"Is It English—Or Ain't It?"—Speaker, Arne O. Lindberg, Washington State University, Pullman, Wash.

THURSDAY, JUNE 12, 1969

Morning Session

R.A.V. Raff, Presiding

8:30 "Radiation Studies at North Carolina State University"—V. T. Stannett
10:30 "The Curing of Coatings on Wood Products by Electron Beam"—P. C. Spencer, Boise Cascade Building Products, Boise, Idaho
Noon LUNCHEON
"Involvement and Motivation in Architectural Education"—Speaker, Dave Scott, Washington State University, Pullman, Wash.

Afternoon Session

Dorothy J. Schecter, Presiding
Washington State University,
Pullman, Wash.

1:30 "Convertible Polymers for Radiation Processing"—D. J. Trecker, Union Carbide Corporation, South Charleston, W. Va.
2:30 "The Effect of Excited Gases on Polymers"—R. H. Hansen, J. P. Stevens and Co., Inc., Garfield, N. J.
3:30 "Effects of Ionizing Radiation on PVC"—A. H. Selker, Tacoma, Wash.
6:30 DINNER
"The Marmes Man"—Speaker, R. Fryxell, Washington State University, Pullman, Wash.

FRIDAY, JUNE 13, 1969

Morning Session

R. V. Subramanian, Presiding
Washington State University,
Pullman, Wash.

8:30 "Chemonuclear and Radiation Chemical Processing—Fundamentals and Present Status of Technology"—Meyer Steinberg, Brookhaven National Laboratory, Upton, N. Y.
9:40 "Process Radiation Using Accelerator Sources"—R. G. Schonberg, SHM Nuclear Corporation, Sunnyvale, Calif.
10:50 "Electron Beam Radiation Applications for the Plastics Industry"—K. H. Morganstern, Radiation Dynamics, Inc., Westbury, Long Island, N. Y.

Noon LUNCHEON
"Research, Industry, and the University"—Speaker, John P. Spielman, Washington State University, Pullman, Wash.

Afternoon Session

R.A.V. Raff, Presiding

1:30 "Industrial Radiation Chemical Process Applications in Existence and of Potential Value"—Meyer Steinberg

2:45 PANEL DISCUSSION—"Commercial Sources of Radiation—A Frank Confrontation": V. T. Stannett, Moderator
Panel Members: J. B. Bradley, K. H. Morganstern, R. G. Schonberg, Meyer Steinberg

5:00 Closing Comments by General Chairman Mark F. Adams

Further details may be obtained from the program chairman Dr. Rudolf A. V. Raff, Polymer Chemist, Chemical Research Section, College of Engineering Research Division, Washington State University, Pullman, Wash. 99163.

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